

The Ce → Pt electron pump across N-rGO for superior hydrogen evolution

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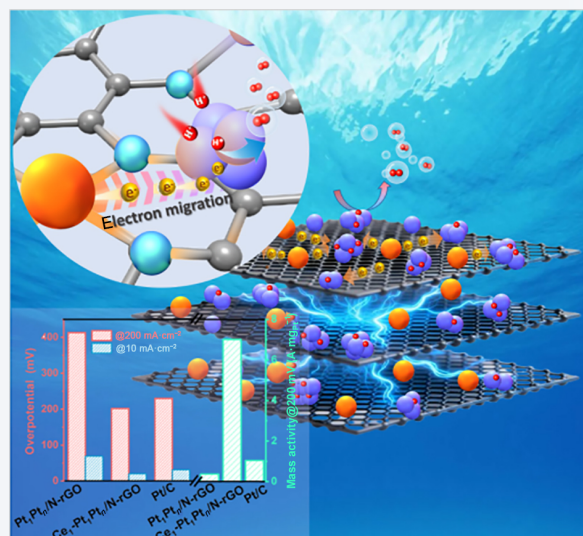
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ABSTRACT: Conventional strategies for enhancing platinum's hydrogen evolution reaction (HER) activity, like alloying or heteroatom-doping, usually suffer from component leaching. We presented a paradigm shift from modifying Pt to remotely engineering its electronic environment. By co-anchoring isolated Ce single atoms, Pt single atoms, and Pt nanoclusters on an N-doped reduced graphene oxide (Ce₁-Pt₁Pt_n/N-rGO) matrix, we constructed an atomic-scale “electron pump”. The architecture enables the unidirectional and spontaneous flow of electrons from the Ce sites, through the N-rGO conduit, into Pt active centers as validated experimentally and theoretically. This remote charge donation optimally tailors the Pt electronic structure, down-shifting its d-band center and optimizing the hydrogen adsorption. The resulting catalyst achieves an ultralow overpotential of 20 mV at 10 mA·cm⁻² and a superior Pt mass activity of 7.0 A·mg_{Pt}⁻¹ at -200 mV, outperforming commercial Pt/C and the Pt₁Pt_n/N-rGO benchmark. Furthermore, it exhibits exceptional stability, retaining an activity of more than 92% after 200 h. This work establishes a novel “remote electron modulator” catalysts, providing a generic pathway for optimizing the performance of noble metals beyond traditional alloy or strain effects.



KEYWORDS: hydrogen evolution reaction (HER), Pt, rare earth, atomic, electronic structure modulation, nitrogen-doped graphene

1 Introduction

The rising global energy demand and the urgent need to mitigate environmental degradation have intensified the search for clean and sustainable energy carriers. Hydrogen, with its high energy density and carbon-neutral combustion profile, stands out as a pivotal candidate for advancing the energy transition [1–3]. Electrochemical water splitting powered by renewable electricity is

the most sustainable route to green hydrogen [4–6]. In this process, platinum (Pt) remains the benchmark catalyst due to its minimal hydrogen evolution reaction (HER) overpotential and superior kinetics. However, its scarcity (0.005 ppm in Earth's crust) and high cost (> 30 USD·g⁻¹) severely hinder large-scale commercial application [7, 8]. Maximizing Pt utilization while enhancing intrinsic activity is therefore a central challenge in electrocatalysis.

Atomically dispersed catalysts (ADCs) have emerged as a promising strategy to address this challenge, offering high atomic utilization and tailorable electronic properties through engineering the local coordination environment and strategic metal-support interactions (MSI) [9–18]. Recent advances have highlighted the potential of integrating single atoms with nanoclusters (≤ 2 nm) by revealing a distinctive synergistic effect for boosting the HER kinetics [19–25]. The combination not only accelerates charge

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transfer but also creates possible multifunctional active sites to facilitate alternative pathways for electron transfer and proton reduction. For example, by co-loading Pt single atoms and small particles (< 2 nm) on mesoporous N-doped carbon nanospheres, Fischer's work demonstrated a clear synergistic HER enhancement: The mesopore-confined Pt_1 and Pt_n entities jointly lower the charge-transfer resistance and optimize *H adsorption, thereby boosting HER activities [26]. Zhang et al. built a hierarchical $Pt_1 + Pt_n/FeOOH@NiFe-LDH$ (LDH = layered double hydroxide) catalyst where Pt single atoms and clusters coexist on NiFe-LDH nanosheets wrapped by amorphous FeOOH. Their experiments and density functional theory (DFT) results show that FeOOH accelerates *H_2O activation, while Pt_1 and Pt_n synergistically tune *H adsorption and H_2 desorption, markedly speeding up HER kinetics [27].

In acidic hydrogen evolution, the rate-limiting step is no longer proton mass transfer but the energy balance of the hydrogen intermediate on the catalyst's surface. Although Pt possesses high intrinsic activity, its d-band center (ϵ_d) lies only ~ 0.2 eV below the Fermi level, resulting in insufficient filling of the antibonding Pt-H * states and a hydrogen adsorption free energy (ΔG_{H^*}) deviating from the thermoneutral optimum [28, 29]. A critical drawback of homonuclear Pt_1Pt_n hybrids is their intrinsically narrow electronic tunability. The negligible electronegativity and electron configuration difference between constituent Pt atoms severely restrict the extent and direction of inter-site charge transfer.

Hetero-atomic engineering (including alloying, core-shell construction, segregation-driven interphase formation, and surface decoration) has proven effective in modulating the electronic structure of active sites [30–32]. Introducing 3d transition metals (e.g., Ni, Co, Fe, and Cu) induces compressive strain and ligand effects that deplete the Pt 5d band and downshift the d-band center to weaken H^* adsorption [33–36]. However, these benefits are inherently transient: The less-noble component is preferentially dissolved under the oxidative/trans-passive potentials encountered in acidic electrolytes [37, 38]. The consequent loss of strain/ligand synergy produces an unpredictable and time-dependent decay in activity that cannot be forecasted from *ex-situ* compositional maps.

Building on the critical role of strong MSI in stabilizing catalysts and enhancing their performance, we propose a paradigm shift from modifying Pt itself to remotely engineering its electronic microenvironment through tailored support design. Extensive efforts have been devoted to engineering carbon-based supports via heteroatom doping, primarily using nonmetallic elements such as N, S, and P, to modulate MSI [39–41]. Metallic dopants, possessing partially occupied and accessible d-orbitals, offer enhanced orbital overlap with Pt and thus provide stronger binding sites and more effective electron transfer. However, studies in this direction remain nascent [42, 43], and the full potential of rationally designed remote electronic modulators has yet to be realized.

We therefore proposed to decouple the electronic modulator from the active site by embedding isolated and non-Pt metal atoms within the support matrix. Such remote sites can dynamically donate electron density, enabling precise and tunable electronic modulation of Pt. Rare-earth (RE) ions are particularly promising candidates because their spatially localized 4f orbitals lie energetically above the Pt 5d band, facilitating spontaneous and unidirectional ligand-to-metal charge transfer. Indeed, prior studies on Pt-RE nanoalloys have demonstrated strong electrocatalytic enhancements stemming from Pt-RE synergy [44–46], yet the

intrinsic mechanism remains obscure due to the synthetic challenges.

Herein, we incorporate isolated RE single atoms (RE_1) into an N-doped reduced graphene oxide (N-rGO) framework that hosts atomically dispersed Pt (Pt_1) and ultrafine Pt clusters (Pt_n , < 2 nm) (denoted as $RE_1-Pt_1Pt_n/N-rGO$). As a prototypical example, $Ce_1-Pt_1Pt_n/N-rGO$ was selected for systematic investigation. Combined experimental and theoretical results reveal that this designed architecture functions as an integrated “atomic electron diode” network: Ce_1 sites act as electron reservoirs, the conductive N-rGO matrix channels electrons directionally toward the Pt active centers, and the Pt sites promote efficient electron transfer to adsorbed protons (H^+). This on-demand charge transfer down-shifts the Pt d-band center, reduces ΔG_{H^*} , and enhances Fermi-level density of states (DOS), yielding an overpotential of 20 mV at 10 mA·cm $^{-2}$ and 7 A·mg $_{Pt}^{-1}$ mass activity at -200 mV vs. reversible hydrogen electrode (RHE), with a current retention of more than 92% after 200 h of cycling. The architecture thus achieves simultaneous optimization of reaction thermodynamics and electron-transfer kinetics, providing a new design concept for ultra-efficient hydrogen-evolution cathodes.

2 Results and discussion

N-rGO was chosen as the substrate to embed Ce single atoms and tiny Pt species for the following reasons: (1) Nitrogen doping lowers the work function of rGO and introduces electron-rich donor states, which facilitate electronic property modulation of the anchored active sites [47–49]. (2) The lone-pair electrons on N atoms enable strong M–N interactions, which stabilize metal species and have been widely adopted as a promising strategy for constructing single-atom catalysts [50, 51]. The synthesis strategy for the $Ce_1-Pt_1Pt_n/N-rGO$ catalysts is depicted in Fig. 1(a). It is widely recognized that the surface of graphene oxide (GO) is negatively charged due to the presence of hydroxyl and carboxyl functional groups. Upon immersed in a solution containing Ce^{3+} ions, these metal cations are uniformly adsorbed onto the GO surface via electrostatic attraction. Subsequent aging in a basic solution containing N-dimethylformamide (DMF) at 70 °C induces *in-situ* hydrolysis. Then, $Pt(NH_3)_4^{2+}$ ions are introduced and electrostatically adsorbed onto the remaining available sites on the GO surface. During the calcination step, DMF serves a dual role as both a nitrogen source for forming N-rGO and a reducing agent to convert adsorbed metal ions into metal atoms. The resulting metal atoms are then anchored by nitrogen sites within the N-rGO matrix. Finally, the as-prepared samples are treated in a 0.5 mol·L $^{-1}$ H_2SO_4 solution to remove any potential oxide species.

Transmission electron microscopy (TEM) images show that the support exhibits a nanosheet morphology (Fig. 1(b)), indicating that the calcination process does not cause structural damage. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) equipped with energy-dispersive X-ray (EDX) spectroscopy elemental mapping was employed to obtain detailed information on composition and structure. As shown in Fig. 1(c) and Fig. S1 in the Electronic Supplementary Material (ESM), uniformly dispersed bright spots as well as nanoclusters can be observed. Statistical analysis of more than 300 clusters reveals that the Pt clusters are predominantly in the size range of 1.4–1.8 nm, with a mean diameter of approximately 1.8 nm, as shown in the histogram of

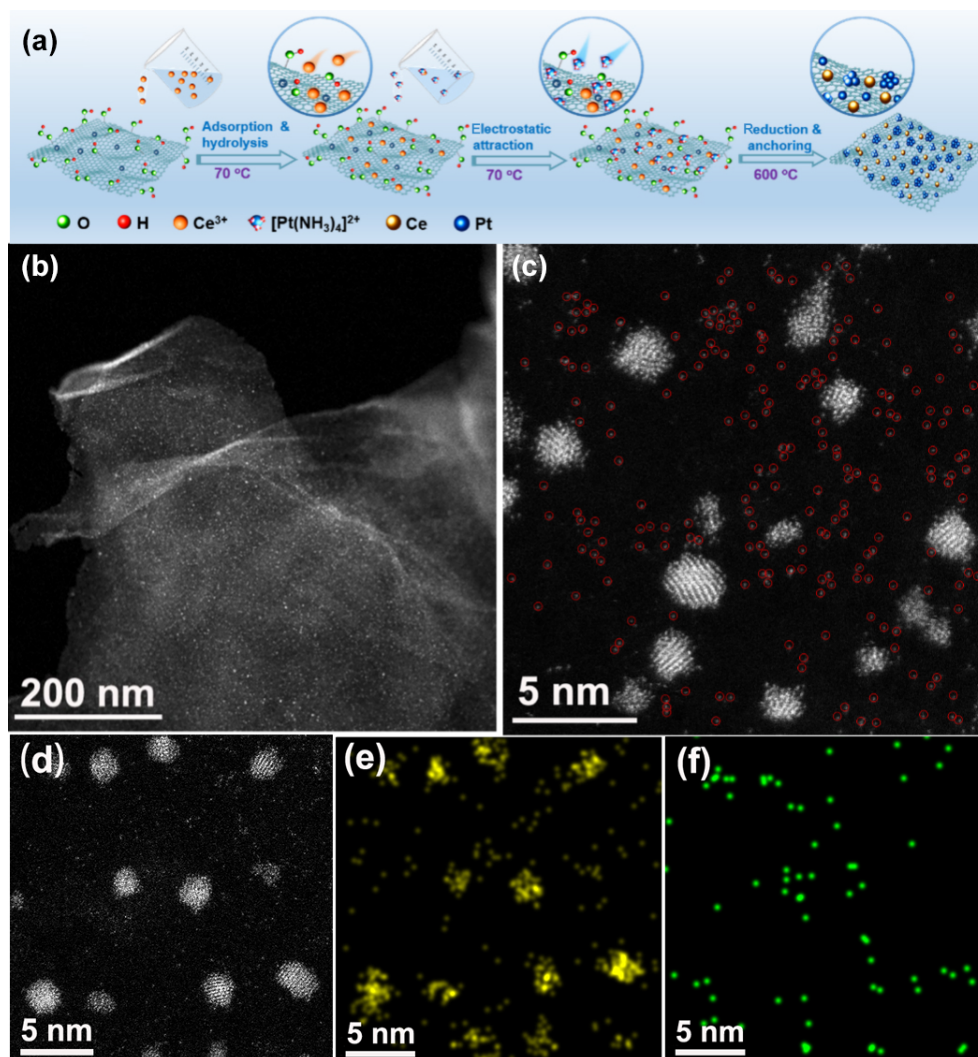


Figure 1 (a) Schematic illustration of the synthesis process for the $\text{Ce}_i\text{-Pt}_t\text{Pt}_n/\text{N-rGO}$ catalyst. (b) Representative low-magnification TEM image. (c) AC-HAADF-STEM image revealing the coexistence of single atoms (circled in red) and nanoclusters. (d) AC-HAADF-STEM image and the corresponding elemental mappings of (e) Pt and (f) Ce.

cluster size distribution (Fig. S1(c) in the ESM). EDX mapping (Figs. 1(d)–1(f)) reveals that the clusters are primarily composed of Pt, while the single atoms consist of both Pt and Ce. These observations certify the successful integration of Ce_i into the $\text{Pt}_t\text{Pt}_n/\text{N-rGO}$ catalysts. The inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis indicates a Pt content of 3.8 wt.% and a Ce content of approximately 0.09 wt.%.

The composition and chemical state of the $\text{Ce}_i\text{-Pt}_t\text{Pt}_n/\text{N-rGO}$ are further characterized using X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum (Fig. S2 in the ESM) reveals the presence of Pt, Ce, C, N and O in the sample. The Ce 3d core-level spectrum (Fig. 2(a)) exhibits spin-orbit doublets characteristic of Ce(III), comprising distinct $3d_{5/2}$ and $3d_{3/2}$ components. The dominant peaks at 886.5 and 905.1 eV originate from the f final state configuration, while the lower-binding-energy satellites at 883.1 and 901.3 eV are attributed to the f configuration [52, 53]. Thus, the XPS features not only confirm the presence of Ce in the $\text{Ce}_i\text{-Pt}_t\text{Pt}_n/\text{N-rGO}$ catalyst but also strongly suggest the ionic Ce^{3+} nature of the Ce single-atom.

To elucidate the effects of Ce_i incorporation, we conducted a comparative XPS analysis of the Pt 4f core-level spectra between $\text{Ce}_i\text{-Pt}_t\text{Pt}_n/\text{N-rGO}$

and $\text{Pt}_t\text{Pt}_n/\text{N-rGO}$. Both samples possess comparable Pt dispersion and cluster size (Figs. S1 and S3 in the ESM), ensuring that any observed spectral differences are due to the Ce_i incorporation. As shown in Fig. 2(b), the Pt 4f peaks of $\text{Ce}_i\text{-Pt}_t\text{Pt}_n/\text{N-rGO}$ are observed at 72.1 ($4f_{7/2}$) and 75.4 eV ($4f_{5/2}$), exhibiting a negative shift of 0.30 eV relative to $\text{Pt}_t\text{Pt}_n/\text{N-rGO}$ (72.4 and 75.7 eV, respectively). This shift indicates an increased electron density at the Pt sites upon Ce_i incorporation. Furthermore, the Pt 4f binding energies in both samples are higher than those of commercial Pt/C, indicating a partial positive charge on Pt sites. This arises from strong covalent Pt-support interactions and the coordinatively unsaturated nature of the Pt_t and Pt_n sites.

The high-resolution N 1s spectra of $\text{Ce}_i\text{-Pt}_t\text{Pt}_n/\text{N-rGO}$ can be deconvoluted into two peaks, as shown in Fig. 2(c). The peak located at 401.7 eV can be assigned to the graphitic N, while the peak at 399.8 eV is a characteristic feature of M–N bonding [54, 55]. The presence of M–N bonds indicates that the metal species (Ce_i and Pt_tPt_n) are stabilized by N-coordination.

X-ray absorption fine structure spectroscopy (XAFS) was employed to probe the local electronic environment. The oxidation state of Ce in $\text{Ce}_i\text{-Pt}_t\text{Pt}_n/\text{N-rGO}$ was analyzed using Ce L₃-edge X-

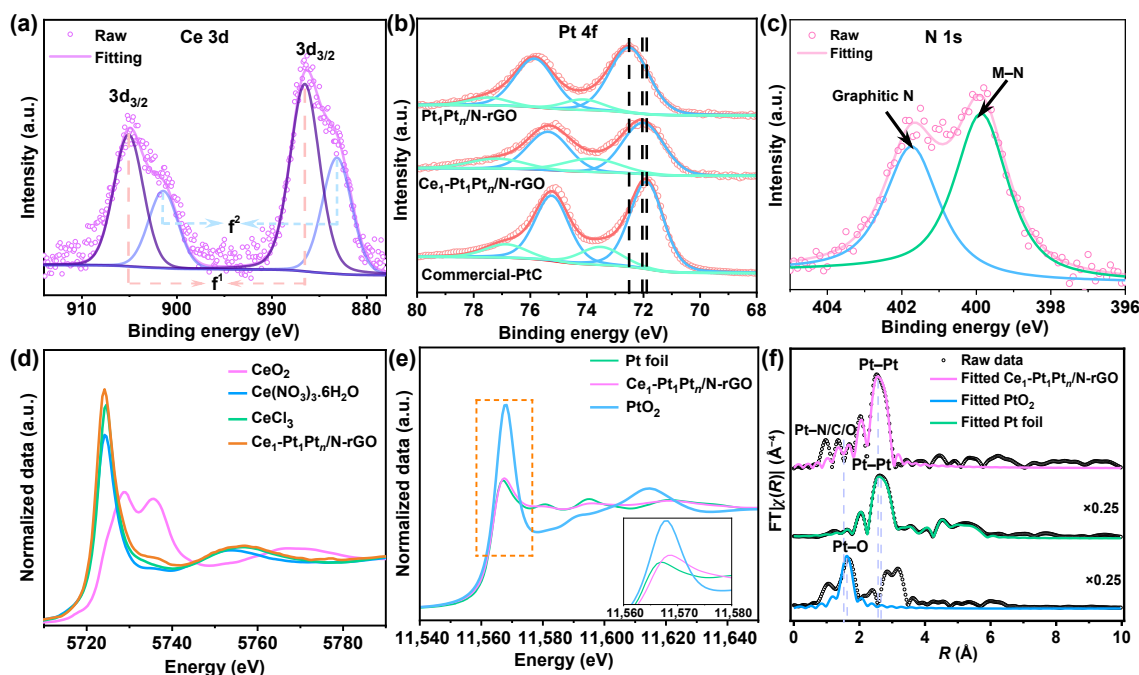


Figure 2 Spectroscopic analysis of the $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ catalyst. (a) Ce 3d XPS spectra. (b) Comparative Pt 4f XPS spectra of $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$, $\text{Pt}_1\text{Pt}_2/\text{N-rGO}$, and commercial Pt/C. (c) N 1s XPS spectrum of $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$. (d) Ce L_3 -edge EXAFS spectra compared with CeO_2 , CeCl_3 , and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ references. (e) Pt L_3 -edge EXAFS spectra and (f) the corresponding FT-EXAFS spectra, along with PtO_2 and Pt foil references.

ray absorption near edge structure (XANES) spectroscopy with CeCl_3 , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and CeO_2 as references. As shown in Fig. 2(d), the Ce L_3 -edge spectrum of $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ closely aligns with those of the Ce^{3+} references (CeCl_3 and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), which are characterized by an intense single white line peak around 5724 eV. This feature is distinct from the spectrum of Ce^{4+} (CeO_2), which exhibits two relatively weaker peaks near 5729 and 5735 eV. These results unambiguously confirm the ionic Ce^{3+} state in the material, thereby substantiating its isolated atomic dispersion, in full consistency with the XPS analysis.

Figure 2(e) compares the normalized Pt L_3 -edge XANES spectra of $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ with respect to the reference materials (Pt foil and PtO_2 powder). The Pt L_3 -edge XANES spectrum of $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ exhibits a white-line intensity slightly higher than that of Pt foil but considerably lower than that of PtO_2 . Since the Pt L_3 -edge intensity corresponds to the electron transition from the $2p_{3/2}$ core level to unoccupied 5d states, it serves as a direct probe of the Pt oxidation state [56, 57]. The observed intensity thereby indicates an oxidation state slightly above zero, which is also consistent with the XPS findings, validating the partially positive oxide states of the Pt species. The k space oscillation curve of the $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ sample (Fig. S4 in the ESM) exhibits a shape similar to that of Pt foil, but with a significantly reduced oscillation amplitude, indicating an altered local atomic arrangement. Extended X-ray absorption fine structure (EXAFS) spectra at the Pt L_3 -edge were analyzed using the Larch package. The amplitude reduction factor (S_0^2) was determined by fitting the Pt foil reference using a metallic Pt model that included relevant single- and multiple-scattering paths. The obtained S_0^2 value was then fixed for all subsequent fits of PtO_2 and $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ samples to ensure consistency in coordination number determination. For the EXAFS fitting of PtO_2 and $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ samples, only first-shell scattering contributions were considered, with the R -space fitting range fixed at 1–3 Å and a k -weight of 3.

Figure 2(f) presents the R -space spectra and the corresponding fitted data derived from the $k_3[\chi(k)]$ -weighted Fourier transform (FT) of the $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ and the reference samples. $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ shows a prominent Pt–Pt coordination peak at approximately 2.56 Å, while weaker peaks at around 1.52 Å are assigned to Pt–C/N/O coordination (Fig. S5 in the ESM). These features indicate the coexistence of Pt single atoms and platinum clusters within the sample. Compared with Pt foil, the relatively low average Pt–Pt coordination number (7.63 ± 0.32) and mean bond length (2.73 ± 0.002 Å) point to the presence of ultrasmall Pt clusters with sizes below 2 nm (Table S1 in the ESM). No Pt–Ce scatters were identified, excluding direct Pt–Ce bonding. These distinct EXAFS characteristics are fully consistent with the AC-HAADF-STEM observations, providing complementary atomic-scale evidence confirming the simultaneous presence of Pt single atoms and nanoclusters in the $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ sample. Furthermore, wavelet transform (WT) analysis of the EXAFS spectra at Ce L -edge (Fig. S6 in the ESM) reveals no Pt–Ce contribution in $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$, corroborating that Ce^{3+} species are predominantly anchored on the N-rGO matrix.

The HER performance of the catalysts was evaluated using a standard three-electrode system in a 0.5 M H_2SO_4 electrolyte with $\text{Pt}_1\text{Pt}_2/\text{N-rGO}$ and commercial Pt/C as comparative benchmarks. The linear sweep voltammetry (LSV) curves (Fig. 3(a)) reveal the superior HER activity of $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$, requiring an overpotential (η) of merely 20 mV to attain the current density (j) of 10 $\text{mA}\cdot\text{cm}^{-2}$. This value is considerably lower than those of commercial Pt/C (31 mV) and $\text{Pt}_1\text{Pt}_2/\text{N-rGO}$ (69 mV). Moreover, the catalytic advantage of $\text{Ce}_1\text{-Pt}_1\text{Pt}_2/\text{N-rGO}$ becomes even more pronounced at high current densities. Its overpotential at 200 $\text{mA}\cdot\text{cm}^{-2}$ is 28 and 210 mV lower than those of Pt/C and $\text{Pt}_1\text{Pt}_2/\text{N-rGO}$, respectively. From a practical standpoint, Pt mass activity, i.e., $\text{A}\cdot\text{mg}_{\text{Pt}}^{-1}$, is an important parameter for evaluating the atomic utilizing efficiency. As summarized in

Fig. 3(b), $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ demonstrates the highest Pt mass activity of $7.01 \text{ A}\cdot\text{mg}_{\text{Pt}}^{-1}$ (at -200 mV vs. RHE), exceeding $\text{Pt}_1\text{Pt}_n\text{/N-rGO}$ ($0.37 \text{ A}\cdot\text{mg}_{\text{Pt}}^{-1}$) and Pt/C ($1.04 \text{ A}\cdot\text{mg}_{\text{Pt}}^{-1}$) by factors of 18.9 and 6.7, respectively, underscoring its exceptional Pt atom efficiency.

To evaluate the intrinsic activity of the Pt active sites, we calculated the turnover frequency (TOF) for each catalyst. The TOF was derived from the current density at an overpotential of -100 mV using Eq. (1)

$$\text{TOF} = \frac{i/(2F)}{n_{\text{Pt}}} \quad (1)$$

where i is the geometric current (A), F is the Faraday constant ($96,485 \text{ C}\cdot\text{mol}^{-1}$), and n_{Pt} is the total amount of Pt (mol) on the electrode (determined by ICP-AES). This calculation assumes that all Pt atoms are accessible active sites, thus providing a conservative lower bound for the intrinsic activity. The $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ catalyst exhibits a TOF of 2.74 s^{-1} at an overpotential of -100 mV , which is approximately 12-fold and 7-fold higher than those of $\text{Pt}_1\text{Pt}_n\text{/N-rGO}$ (0.23 s^{-1}) and Pt/N-rGO (0.40 s^{-1}), respectively. These results clearly demonstrate that the introduction of Ce single atom plays a crucial role in the performance improvement.

To gain further insight into the underlying mechanism, we synthesized $\text{Ce}_1\text{/N-rGO}$ and evaluated its HER performance both individually and as a physical mixture with $\text{Pt}_1\text{Pt}_n\text{/N-rGO}$, while keeping the Ce amount identical to that in the $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ catalyst. As shown in Fig. S7 in the ESM, $\text{Ce}_1\text{/N-rGO}$ alone exhibits negligible HER activity. When the physically mixed $\text{Ce}_1\text{/N-rGO} + \text{Pt}_1\text{Pt}_n\text{/N-rGO}$ sample was tested, the activity was even lower than that of $\text{Pt}_1\text{Pt}_n\text{/N-rGO}$ alone. Maintaining the Ce/Pt molar ratio via physical mixing inevitably introduced additional N-rGO, which may increase contact resistance and thus lead to a slight deterioration in activity. Importantly, no synergistic enhancement was observed, indicating that simple physical contact fails to replicate the catalytic benefits of the covalently integrated $\text{Ce}_1\text{-}$

$\text{Pt}_1\text{Pt}_n\text{/N-rGO}$ structure. Given that EXAFS data reveal the absence of direct Pt–Ce bonding in $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$, we attribute the dramatically enhanced intrinsic catalytic activity of the Pt sites to remote electronic regulation by the Ce single atoms.

Electrochemical kinetics analyses further corroborate the superior HER performance of $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$. As depicted in Fig. 3(c), the Tafel slope of $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ is $22.58 \text{ mV}\cdot\text{dec}^{-1}$, substantially lower than those of $\text{Pt}_1\text{Pt}_n\text{/N-rGO}$ ($58.78 \text{ mV}\cdot\text{dec}^{-1}$) and commercial Pt/C ($33.83 \text{ mV}\cdot\text{dec}^{-1}$), indicating more favorable reaction kinetics. This enhancement is further supported by electrochemical impedance spectroscopy (EIS). As shown in Fig. 3(d), the charge transfer resistance (R_{ct}) of $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ is determined to be only 2.01Ω , which is dramatically lower than 9.22Ω measured for the Ce-free counterpart ($\text{Pt}_1\text{Pt}_n\text{/N-rGO}$). This sharp decrease in R_{ct} upon Ce incorporation directly confirms the pivotal role of Ce_1 in establishing a highly efficient electron transfer pathway to the Pt active sites. The notably enhanced activity and faster kinetics of $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ relative to $\text{Pt}_1\text{Pt}_n\text{/N-rGO}$ highlight the significant synergistic interplay between Pt and Ce.

$\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ also demonstrates outstanding operational stability, as verified by both chronopotentiometric and accelerated durability tests. It retained 92.04% of its initial current after 200 h of continuous operation at -0.5 V (vs. RHE), vastly outperforming Pt/C and $\text{Pt}_1\text{Pt}_n\text{/N-rGO}$, which lost 21.56% and 55.6% of their activity within just 8 h, respectively (Fig. 3(e)). This stability was further underscored by an overpotential increase of mere 7 mV to achieve a current density of $200 \text{ mA}\cdot\text{cm}^{-2}$ after 10,000 CV cycles, a value dramatically lower than that of Pt/C (57 mV , Fig. 3(f)). The exceptional stability originates from the synergistic interplay between Ce_1 , Pt_1 , and Pt_n . The hybrid structure provides enhanced conductivity and a favorable electronic environment that sustains catalytic activity. The post-stability catalyst was further characterized by HAADF-STEM and XPS. The HAADF-STEM images (Fig. S8 in the ESM) reveal that the catalyst retains a structure consisting of both single atoms and clusters. The cluster

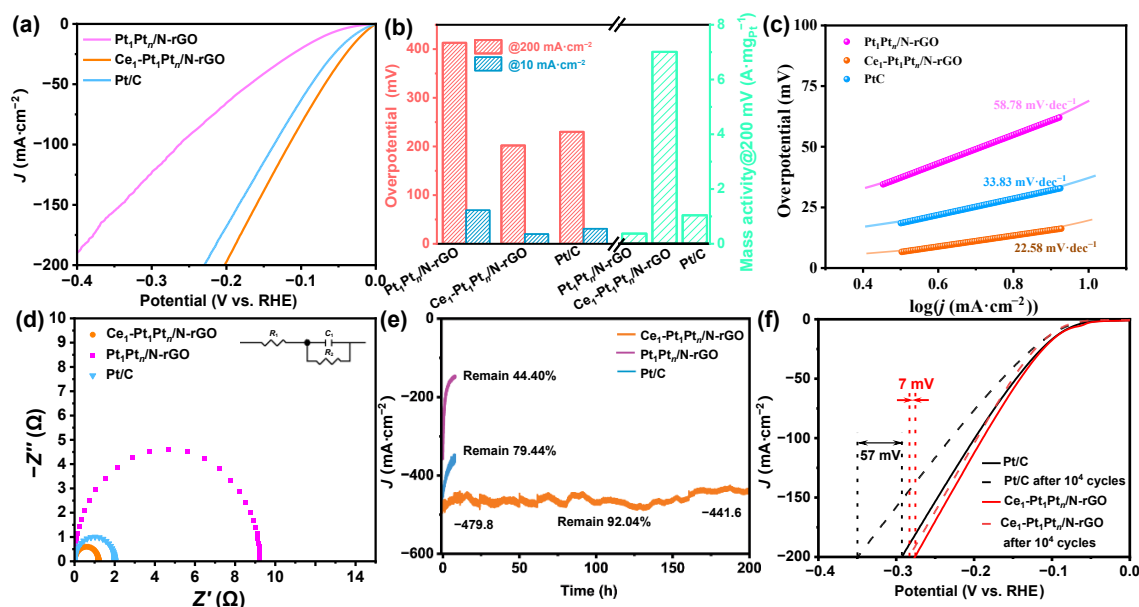


Figure 3 Electrochemical performance of the $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ catalyst for the HER in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte at a sweep rate of $5.0 \text{ mV}\cdot\text{s}^{-1}$ with commercial Pt/C (20 wt.%) and $\text{Pt}_1\text{Pt}_n\text{/N-rGO}$ as the references. (a) LSV curves normalized by geometric surface area of the electrode. (b) Overpotentials at 10 and $200 \text{ mA}\cdot\text{cm}^{-2}$ and mass activity at -200 mV vs. RHE. (c) Tafel plots derived from the LSV curves in (a). (d) Potentiostatic electrochemical impedance spectra. (e) Chronoamperometric stability test. (f) LSV curves before and after 10,000 CV cycles for $\text{Ce}_1\text{-Pt}_1\text{Pt}_n\text{/N-rGO}$ and commercial Pt/C.

size distribution remains predominantly in the range of 1.4–1.8 nm, almost identical to that observed before the stability test, and no large aggregates were observed after the long-term test. The absence of cluster coarsening and the clear visibility of single atoms confirms the structural stability of the catalyst. XPS analysis provides complementary evidence. As shown in Fig. S9(a) in the ESM, the Pt 4f binding energy shifts by less than 0.1 eV after the test, and no additional Pt species and no additional Pt species were detected, indicating that the chemical state of Pt is largely preserved. The Ce 3d spectra (Fig. S9(b) in the ESM) show that Ce remains exclusively in the Ce^{3+} state, with no detectable Ce^{4+} peaks, suggesting that the residual Ce species have not been oxidized to CeO_2 during HER. These results demonstrate that the N-doped rGO support serves as a robust anchor, effectively suppressing the migration and agglomeration of metal species, and thereby preserving the catalytically active structure during prolonged operation.

To gain atomic-level insight into the origin of the superior HER

performance, we conducted first-principles DFT calculations within the generalized-gradient approximation. Guided by established literature [58], the Pt_1 and Ce_1 single atoms were modeled as planar M-N_4 moieties embedded in an N-doped graphene framework. A Pt_{12} icosahedral cluster was positioned adjacent to the Pt_1 site to represent the $\text{Pt}_1\text{Pt}_{12}$ dual-site configuration, thereby capturing the synergistic interaction between atomic dispersion and cluster sites. Figure S10 in the ESM displays the established structure models of $\text{Pt}_1/\text{N-rGO}$, $\text{Pt}_1\text{Pt}_{12}/\text{N-rGO}$, and $\text{Ce}_1\text{-Pt}_1\text{Pt}_{12}/\text{N-rGO}$ with varied Ce–Pt distances.

The Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) was computed to evaluate the activity of potential active sites. As shown in Fig. 4(a), the ΔG_{H^*} value for the isolated Pt_1 site is highly positive (+1.54 eV), indicating thermodynamically unfavorable adsorption of the hydrogen intermediate (H^*). In contrast, H^* adsorption on the Pt_{12} cluster is substantially stronger, with a negative ΔG_{H^*} value of −0.58 eV. In the $\text{Pt}_1 + \text{Pt}_{12}$ dual-site configuration, in contrast, the H^* adsorption on the Pt_{12} cluster is substantially stronger, with a

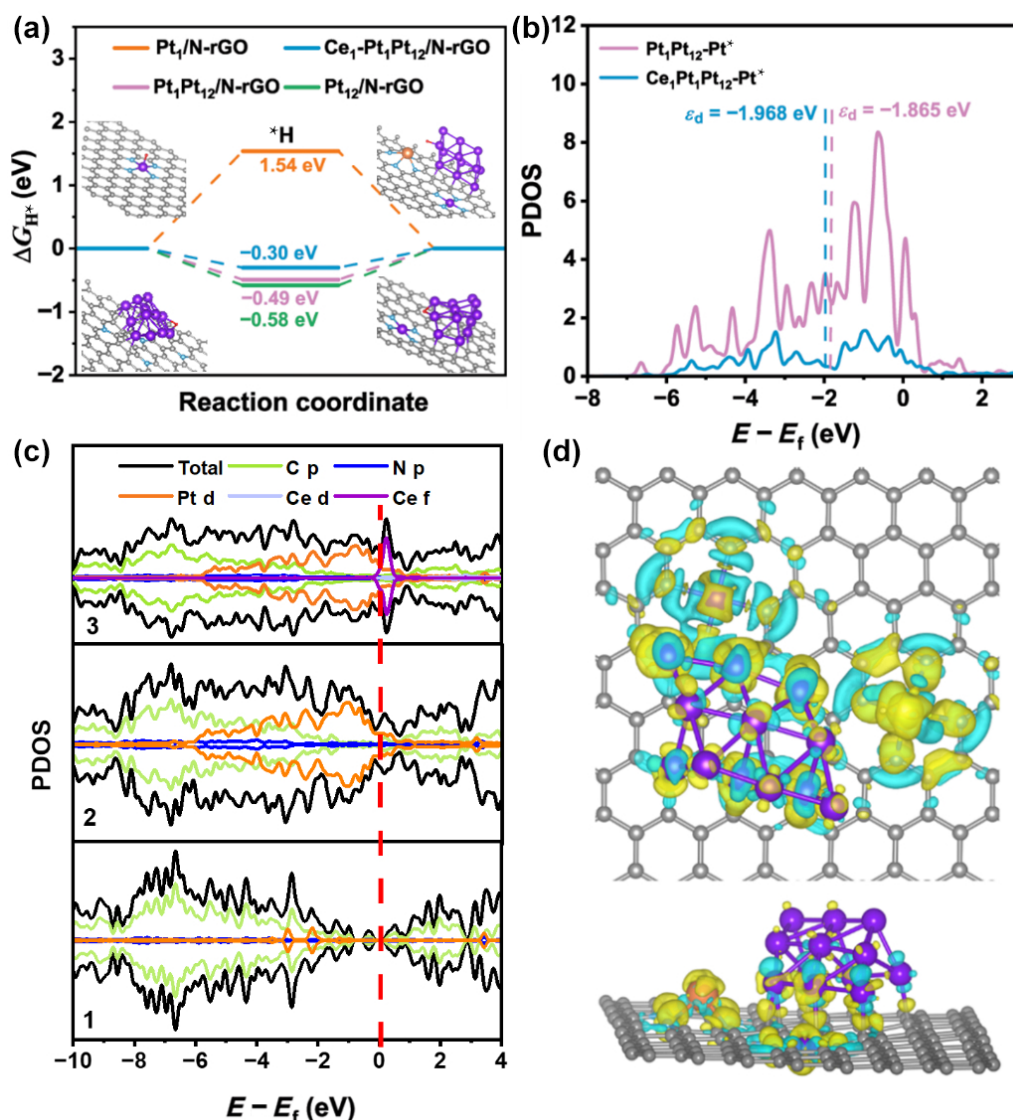


Figure 4 DFT calculations and electronic structure analysis of $\text{Ce}_1\text{-Pt}_1\text{Pt}_{12}/\text{N-rGO}$ and the references. (a) calculated hydrogen adsorption free energy diagrams (ΔG_{H^*}). Insets: corresponding optimized structures (gray, blue, orange, purple, and red balls represent C, N, Ce, Pt, and H atoms, respectively). (b) PDOS of the Pt^* 5d states in $\text{Ce}_1\text{-Pt}_1\text{Pt}_{12}$ and $\text{Pt}_1\text{Pt}_{12}$. (c) Total PDOS curves for $\text{Pt}_1/\text{N-rGO}$ (curve 1), $\text{Pt}_1\text{Pt}_{12}/\text{N-rGO}$ (curve 2), and $\text{Ce}_1\text{-Pt}_1\text{Pt}_{12}/\text{N-rGO}$ (curve 3), showing the variation of electron density across the energy scale, particularly around the Fermi level. (d) 3D charge-density difference diagram of $\text{Ce}_1\text{Pt}_1\text{Pt}_{12}/\text{N-rGO}$ (top: front view, and bottom: side view).

negative ΔG_{H^*} value of -0.49 eV. Although this represents a slight weakening of adsorption relative to the isolated Pt_{12} cluster, the binding remains too strong. This suggests that the Pt single atom alone provides insufficient electronic modulation of the Pt cluster to achieve optimal H^* binding. Remarkably, upon incorporating a proximal Ce_1 atom, ΔG_{H^*} is further tuned to 0.30 eV. According to Nørskov's thermodynamic descriptor for optimal HER activity, an ideal HER electrocatalyst should exhibit a small $|\Delta G_{\text{H}^*}|$ value to ensure thermoneutral adsorption-desorption of the H^* intermediate [59]. Therefore, the correlation between HER activity and the calculated ΔG_{H^*} values confirms that the synergistic interaction among Pt_1 , Ce_1 , and Pt cluster, particularly the incorporation of Ce_1 , optimizes the Pt-H interaction.

Partial density of states (PDOS) analysis was further employed to investigate the d-band center of the active Pt site (denoted as Pt^*), which corresponds to the Pt site where H is adsorbed during the HER. The results reveal that the Ce_1 introduction downshifts the d-band center of Pt^* from -1.865 to -1.968 eV (Fig. 4(b)). This shift lowers the occupancy of antibonding states in the Pt-H interactions, thereby weakening the Pt-H binding strength and, in turn, accelerating the HER kinetics in accordance with the established d-band theory.

Additionally, the calculated total density of states reveals that the electronic synergy between Pt and Ce also improves the electrical conductivity of the material. Specifically, the Pt_1Pt_n cluster exhibits a higher electron density near the Fermi level (E_{F}) compared to a Pt single atom, while the incorporation of Ce_1 induces a further accumulation of electronic states in this region (Fig. 4(c)). The enrichment of the DOS near E_{F} markedly reduces the electrical resistance of the $\text{Ce}_1\text{-Pt}_1\text{Pt}_n/\text{N-rGO}$ composite, as experimentally validated by the lowered charge transfer resistance observed in electrochemical impedance spectroscopy. Consequently, this facilitated electron transfer further speeds up the HER kinetics.

Charge-density difference diagram (Fig. 4(d)) and Bader charge analysis indicate both Pt_1 and Ce_1 act as electron donors, transferring electron density to the N-doped rGO scaffold, whereas the Pt_{12} cluster serves as an electron acceptor, accumulating excess negative charge. This electron enrichment of the Pt_{12} cluster promotes the reduction of adsorbed hydrogen species (H^*), thereby optimizing ΔG_{H^*} . In the $\text{Pt}_1\text{Pt}_{12}/\text{N-rGO}$ system, the Pt_{12} cluster gains 0.146 e, as revealed by Bader charge analysis. Upon the introduction of a Ce single atom in close proximity to the Pt_{12} cluster, the accumulated charge on Pt_{12} increased markedly to 0.419 e. This substantial increase in electron accumulation highlights the critical role of the Ce_1 site in modulating the electronic state of the Pt active ensemble. Notably, the Ce single atom is not directly bonded to Pt, as revealed by the EXAFS spectra analysis discussed above, suggesting that the electron transfer is mediated by the N-rGO support, which is also verified by the charge-density difference diagram in Fig. 4(d) and Bader charge analysis. Bader charge analysis further reveals that, within the N-rGO matrix, C atoms donated electrons while N atoms accepted electrons. It is reasonable to conclude that the N-rGO matrix acts as an electron bridge, accepting electrons from Ce and redistributing them toward the Pt clusters.

To further validate this remote electronic modulation across the N-rGO matrix, we performed Bader charge analysis on $\text{Ce}_1\text{-Pt}_1\text{Pt}_{12}/\text{N-rGO}$ models with varying Ce-Pt distances to probe the distance dependence of the electronic interaction. When the distance between the Ce single atom and the Pt_{12} cluster is 4.1 Å, the Pt_{12} cluster gains 0.419 e. When the distance is extended to

approximately 5.4 Å, the charge gained by Pt_{12} decreases slightly to 0.377 e, yet remains substantially higher than that in the absence of Ce. These results demonstrate that electron transfer from Ce to the Pt cluster persists over an extended distance, providing strong evidence for the remote electronic regulation effect of Ce_1 . The related structure models are shown in Fig. S10 in the ESM. It can be reasonably concluded that the charge redistribution leads to an electron-rich Pt_{12} cluster, which optimizes H^* adsorption behavior, consistent with the negative shift in the Pt binding energy observed by XPS after Ce_1 incorporation.

Based on the above analysis, the exceptional HER performance of the $\text{Ce}_1\text{-Pt}_1\text{Pt}_n/\text{N-rGO}$ electrocatalyst arises from two synergistic effects enabled by the incorporation of Ce single atom. (1) Optimization of reaction thermodynamics via electronic modulation. Ce_1 serves as a key electron donor, triggering a significant electron redistribution that enriches the Pt_n cluster with electron density and downshifting its d-band center. This electronic modulation weakens Pt-H binding and brings ΔG_{H^*} closer to thermoneutral, thereby accelerating the reaction kinetics by facilitating both H^* adsorption and H_2 desorption. (2) Enhancement of charge transfer. The synergistic electronic interplay among Pt_1 , Pt_n , and Ce_1 sites leads to a pronounced increase in the density of states near the Fermi level. This electronic enrichment markedly improves the electrical conductivity of the catalyst, which is experimentally corroborated by the observed reduction in charge transfer resistance. The resulting facilitation of electron transfer subsequently accelerates the overall HER kinetics.

3 Conclusions

In summary, we successfully engineered a $\text{Ce}_1\text{-Pt}_1\text{Pt}_n/\text{N-rGO}$ electrocatalyst that demonstrates exceptional performance for the HER in acidic media. This catalyst achieves a low overpotential of only 20 mV at 10 mA·cm $^{-2}$, surpassing commercial Pt/C (31 mV) and $\text{Pt}_1\text{Pt}_n/\text{N-rGO}$ (69 mV), alongside a Pt mass activity 6.7 and 18.9 times higher, respectively. Crucially, it exhibits outstanding durability with 92.04% current retention over 200 h of continuous operation at -0.5 V. Combined experimental and theoretical analyses unveil that the incorporated Ce single atoms act as electron donors, directing a flow of electrons via the N-rGO support to the Pt nanoclusters. This targeted electronic modulation optimizes the Pt d-band center and accelerates reaction kinetics, creating a synergistic effect that concurrently elevates both activity and stability. Our findings provide a profound understanding of electronic metal-support interactions and introduce a versatile design concept utilizing rare-earth single atoms for the precise electronic engineering of electrocatalysts.

Electronic Supplementary Material: Supplementary material (experimental procedures, additional STEM/XPS/EXAFS data, electrochemical results, and DFT computational details) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908803>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

D.-F. Z.: Conceptualization, supervision, data curation, project administration, writing manuscript, methodology, funding acquisition. Y.-Q. L.: Validation, experimental design, visualization. H.-Z. B.: Investigation, experimental design. D. H. C. W.: Data analysis. L.-L. Z.: Investigation. W.-C. C.: Investigation. L.-D. L.: Conceptualization, methodology, funding acquisition. F. R. W.: Methodology, formal analysis, writing manuscript. Y. G.: Funding acquisition. J.-X. K.: Methodology, resources, supervision. All the authors have approved the final manuscript.

Use of AI statement

None.

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