

Alkaline earth metals induced electron transfer to Pt single-atom on carbon nitride toward boosting photocatalytic H₂ production

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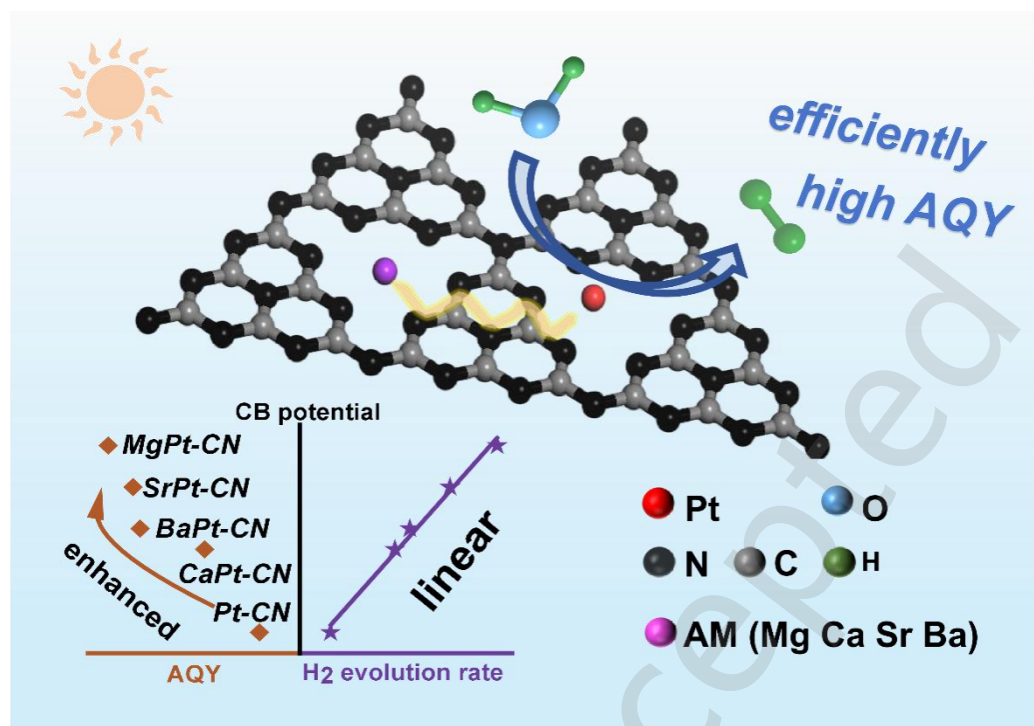
Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94908980>
<https://www.sciopen.com/journal/1998-0124> on Jun. 29, 2026

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TABLE OF CONTENTS (TOC)



The incorporation of alkaline earth metals (Mg, Ca, Sr and Ba) optimized the electronic properties of Pt single atoms on carbon nitride, resulting in a 3.3 to 7.2-fold enhancement in photocatalytic H₂ production compared with unmodified Pt-CN.

Alkaline earth metals induced electron transfer to Pt single-atom on carbon nitride toward boosting photocatalytic H₂ production

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Received: 29 March 2026; Revised: 2 June 2026; Accepted: 29 June 2026

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 Cite this article: *Nano Research*, 2026, 19, 94908980 <https://doi.org/10.26599/NR.2026.94908980>

ABSTRACT: Regulating electronic configuration to fully exploit the potential of Pt single atoms for efficient photocatalytic hydrogen production is of great significance, but remains challenging. Herein, we report alkaline earth metals (AM) modified atomically dispersed Pt sites on graphitic carbon nitride (CN) for photocatalytic H₂ production. The results of XPS, XAFS and DFT calculation demonstrate that in these AMPt-CN (AM: Mg, Ca, Sr and Ba) catalysts, the incorporation of AM effectively increases the electron density of Pt single-atom and decreases the d-band center of Pt, concurrently reducing the free energy barrier for the hydrogen evolution reaction. Additionally, fs-TAS and photoelectric performance tests of catalysts reveal concurrent improvements in light absorption and charge separation efficiency with alkaline earth metal doping. Consequently, the optimized AMPt-CN achieve a remarkable hydrogen production rates of 2.79 (MgPt-CN), 1.55 (CaPt-CN), 2.12 (SrPt-CN) and 1.34 (BaPt-CN) mol g_{Pt}⁻¹ h⁻¹ with an high apparent quantum yield of 21.7%, 18.1%, 18.9% and 10.8%, respectively, superior to most of the reported carbon nitride based Pt single-atom catalysts. Noteworthy, together with energy band structure results, a prominent linear relationship between the hydrogen evolution activity and the corresponding conduction band potentials is established. These findings reveal a new perspective for in-depth comprehension of the role of alkaline earth metals in adjusting electronic properties of Pt single-atom catalysts for promoting photocatalytic performance.

KEYWORDS: Pt single atoms, graphitic carbon nitride, alkaline earth metals, d-band center control, photocatalytic hydrogen evolution

1 Introduction

Solar-driven photocatalytic water splitting for the production of clean hydrogen is a promising and sustainable approach to address pressing environmental issues and energy crisis. Up to now, a variety of photocatalysts have been developed for high-efficiency hydrogen evolution reaction (HER) [1-5]. Among these, graphitic carbon nitride (g-C₃N₄) is expected to be an ideal candidate owing to its proper bandgap and band structure, excellent chemical stability and low cost. Unfortunately, bulk g-C₃N₄ suffers from inefficient charge separation, leading to the H₂ production performance far from the theoretical predictions [6]. Therefore, various strategies have been proposed to improve the photocatalytic performance, such as elemental doping [7], defect engineering [8], heterostructure constructing [9], metal loading [10], among which, integrating g-C₃N₄ with metals to construct single-atom catalysts (SACs) is more expected [11], because of their high atomic utilization, superior selectivity and strong metal-support interactions [12].

Graphitic carbon nitride has gained popularity as superb supports of single-atom metals due to its abundant pyridine-like N atoms, which can powerfully anchor isolated metal atoms [13]. Especially, the emerging Pt SACs on g-C₃N₄ have shown significantly more efficient and durable H₂ evolution activity compared to Pt nano-cocatalysts [14], and extensive research has been focused on increasing the loading of Pt SACs to obtain higher H₂ evolution [15, 16]. However, high metal loading could promote the aggregation of Pt single atoms to Pt clusters due to

their high surface free energy [17, 18], consequently degrading the HER performance. More importantly, simply increasing loading may increase the number of accessible active sites, but it does not fundamentally overcome the intrinsic limitation of Pt SACs, as their catalytic performance is primarily governed by the local electronic structure and coordination environment of Pt atoms. Thus, precise modulation of isolated Pt sites, rather than merely increasing Pt loading, is essential for advancing Pt SACs toward efficient photocatalytic HER, but remains challenging.

The strategic manipulation of electronic structure via electron transfer presents a promising and controllable approach to adjust the d-band structure of Pt, which can regulate the adsorption of reaction intermediates, lower the energy barrier, and facilitate the hydrogen evolution reaction [19, 20]. To this end, leveraging the differences in work functions and valence electron counts, transition metal elements have been introduced for adjusting the surface electronic density of Pt sites, as demonstrated for Au [21], Co [22] and Ag [23] in previous reports. Alkaline earth metals (Group IIA), characterized by their ns² valence electron configuration, have been employed to enhance light absorption and carrier separation of photocatalysts [24-27]. However their potential for modifying the electronic structure of active sites has been overlooked. Their potential stems from their low electronegativity and tendency to lose valence electrons to form stable divalent cations with noble-gas-like electronic configurations, which enables alkaline earth metals to act as potent electron donors [28], exerting deterministic control over

the electron density of Pt [29, 30]. Compared with many transition metals, alkaline earth metals generally exhibit a larger electronegativity difference relative to Pt, which may favor more pronounced charge redistribution around the Pt–N sites through the carbon nitride framework. This provides a distinct electronic modulation mode for regulating the electronic structure of Pt single atoms. Besides, the inherent absence of available d-orbital in alkaline earth metals confines their capacity to adsorb reaction intermediates in most cases, thereby eliminating undesired competitive reactions with the Pt active sites. Furthermore, alkaline earth metals are low-cost, environmentally friendly and readily available [31]. These advantages make them promising candidates for optimizing the charge distribution of Pt single atoms. To the best of our knowledge, the effect of alkaline earth metals on the electronic properties of Pt SACs remains unexplored from either a theoretical or experimental perspective.

Herein, a series of alkaline earth metals (AM: Mg, Ca, Sr and Ba) modified atomically dispersed Pt SACs on g-C₃N₄ were fabricated for enhanced photocatalytic hydrogen production. The incorporation of alkaline earth metals effectively modulates the electronic structure of Pt atoms, promoting electron aggregation at the Pt active sites and inducing a significant upward shift of the conduction band. Consequently, MgPt-CN, CaPt-CN, SrPt-CN and BaPt-CN exhibited markedly promoted H₂ evolution activity of 2.79, 1.55, 2.12 and 1.34 mol g_{Pt}⁻¹ h⁻¹, with elevated apparent quantum yield (AQY) at 420 nm of 21.7%, 18.1%, 18.9% and 10.8%, respectively, compared with those of Pt-CN (0.43 mol g_{Pt}⁻¹ h⁻¹ with an AQY of 4.6%). Furthermore, the hydrogen evolution activities showed a tight linear correlation with the CB potentials of the corresponding catalysts. Multiple characterizations and DFT calculations were adopted to investigate and elucidate the reasons for enhanced catalytic hydrogen evolution of AMPt-CN. The results obtained provide a valuable reference for promoting the photocatalytic hydrogen production activity of Pt SACs through tuning their electronic structure.

2 Experimental

2.1 Materials

Urea (Macklin, AR), Mg(NO₃)₂·6H₂O (Kemio, AR), Ca(NO₃)₂·4H₂O (Sinopharm, AR), Sr(NO₃)₂ (Haohua, AR), Ba(NO₃)₂ (Sinopharm, AR), Ar and N₂ (Yuanzheng, 99.99%), triethanolamine (TEOA, Sinopharm, AR), H₂PtCl₆·6H₂O (Aladdin, AR), ethanol (Sinopharm, AR), Na₂SO₄ (Sinopharm, AR).

2.2 Synthesis of AMPt-CN

CN was prepared with a classic method. A certain amount of urea was put in a covered crucible and heated in a muffle furnace at 550 °C for 120 min with a 8 °C/min heating rate. Firstly, 230 mg CN and metal nitrates (27 mg Mg(NO₃)₂·6H₂O or 29.1 mg Ca(NO₃)₂·4H₂O or 22.3 mg Sr(NO₃)₂ or 27.6 mg Ba(NO₃)₂) were added into 10 ml deionized water and the mixed solution was ultrasonicated for 15 min. The suspension was kept in liquid nitrogen, followed by freeze drying. The mixture was heated at 500 °C for 200 min with a 2.5 °C/min heating rate under Ar. Then photodeposition method was employed to further synthesize AMPt-CN. 60 mg as-synthesized sample was dispersed in 90 ml deionized water and 10 ml TEOA by ultrasonication for 5 min. Next 270 μl H₂PtCl₆ solution (10 mg

ml⁻¹) was added in above suspension under constant stirring. After the vessel was thoroughly evacuated and filled with N₂ for 10 min, respectively, a visible-light irradiation provided by a 300 W Xe lamp was cast on the continuous stirring reaction mixture for 30 min. Afterwards the suspension was filtered, washed with deionized water and ethanol sequentially, and then dried under vacuum at 60 °C. Finally the dried products was annealed at 450 °C for 120 min with a 3 °C/min heating rate under Ar to obtain AMPt-CN (AM=Mg, Ca, Sr, Ba).

2.3 Synthesis of AM-CN, Pt-CN and CN-D

AM-CN was synthesized using a procedure similar to that utilized for AMPt-CN preparation, except that H₂PtCl₆ solution was omitted in photodeposition process.

Pt-CN was synthesized using a procedure similar to that utilized for AMPt-CN preparation, except that metal nitrate was omitted in the initial freeze-drying process.

CN-D was synthesized using a procedure similar to that utilized for AMPt-CN preparation, without the use of metal nitrates in the initial freeze-drying process and H₂PtCl₆ solution in photodeposition process.

2.4 Photocatalytic activity experiment

The photocatalytic H₂ evolution of catalysts was performed using Pyrex top-irradiation reaction vessel coupled to a closed glass-gas system. 10 mg photocatalyst, 90 ml deionized water and 10 ml TEOA were added into glass reactor. Subsequently, the reaction solution was evacuated 30 min to remove air completely. The temperature of the solution was kept at 5 °C through circulating cooling water system during the reaction. The light source was a 300 W xenon lamp (λ > 420 nm). And the H₂ amount was determined using a gas chromatograph with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column using Ar as the carrier gas. The wavelength-dependent apparent quantum yield (AQY) was measured using the Xe lamp equipped with band-pass filters of different wavelengths (420, 435, 450, 475 and 520 nm).

2.5 Photoelectrochemical measurements

Electrochemical tests were performed on a CHI660E electrochemical workstation (Chen Hua, China) by using a standard three-electrode system consisting of sample-coated indium-doped tin oxide (ITO) glass (working electrode), Pt plate (counter electrode), and Ag/AgCl electrode (reference electrode). The electrolyte is Na₂SO₄ (0.5 M). A 100 W xenon lamp was used as the light source.

3 Results and discussion

The AMPt-CN catalysts were prepared via a two-step pyrolysis method (Fig. S1 in the Electronic Supplementary Material (ESM)). The metal loadings of the as-prepared samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis, and the results were summarized in Table S1 in the ESM. The X-ray diffraction (XRD) patterns of all samples showed two distinct diffraction peaks at approximately 13.7° and 27.8° (Fig. S2 in the ESM), indexed to the (100) and (002) planes of typical g-C₃N₄, respectively. No additional peaks related to metal or metal oxide nanoparticles were detected in all samples, suggesting that Pt and alkaline earth metals were likely atomically dispersed within g-C₃N₄. The Fourier transform infrared (FTIR) spectra were shown in Fig. S3 in the ESM. The characteristic peaks centered at 810, 1200-1700 and 3000-3300 cm⁻¹ are assigned to the

bending vibrations of heptazine units, the stretching vibrations of aromatic C–N heterocycles, and the stretching vibrations of –NH_x groups, respectively [32, 33], indicating the preserved fundamental structure of g-C₃N₄ after the incorporation of alkaline earth and Pt atoms. The Brunauer-Emmett-Teller (BET) measurements revealed that while the N₂ adsorption-desorption isotherms and pore size distributions of CN-D and AMPt-CN were similar, the specific surface area increased after metal doping (Figs. S4-S6 in the ESM). This increase in surface area is conducive to exposing more active sites for photocatalytic reactions [34].

The morphology of the prepared catalysts was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). According to SEM images, CN-D (Fig. S7(a) in the ESM) and Pt-CN (Fig. S7(b) in the ESM) exhibited a representative randomly arranged 2D nanosheet morphology and this microstructure remained intact after the introduction of alkaline earth metals (Figs. S7(c-f) in the ESM). The TEM

layered structure without observable granular aggregates, demonstrating the high dispersion of Pt sites in all samples. Moreover, energy-dispersive X-ray spectroscopy (EDS) elemental mappings (Figs. S10-S14 in the ESM) confirmed the presence and uniform distribution of Pt and alkaline earth metals throughout the g-C₃N₄ substrate. Furthermore, the dispersion of atomic Pt in the Pt-CN sample was confirmed by aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) (Fig. 1(c)). The bright spots circled in red unambiguously proved that Pt presented mainly as single atoms. The elemental distribution mapping shown in Fig. 1(d) indicated that Pt, N, and C were distributed homogeneously throughout the entire architecture. As a representative, MgPt-CN sample was selected to explore the dispersion of alkaline earth metals. No Mg nanoparticles or clusters were observed in Fig. 1(e), confirming the atomic dispersion of Mg species. Meanwhile, Pt (circled in red circles in Fig. 1(e)) still remained in the form of single atoms, and the

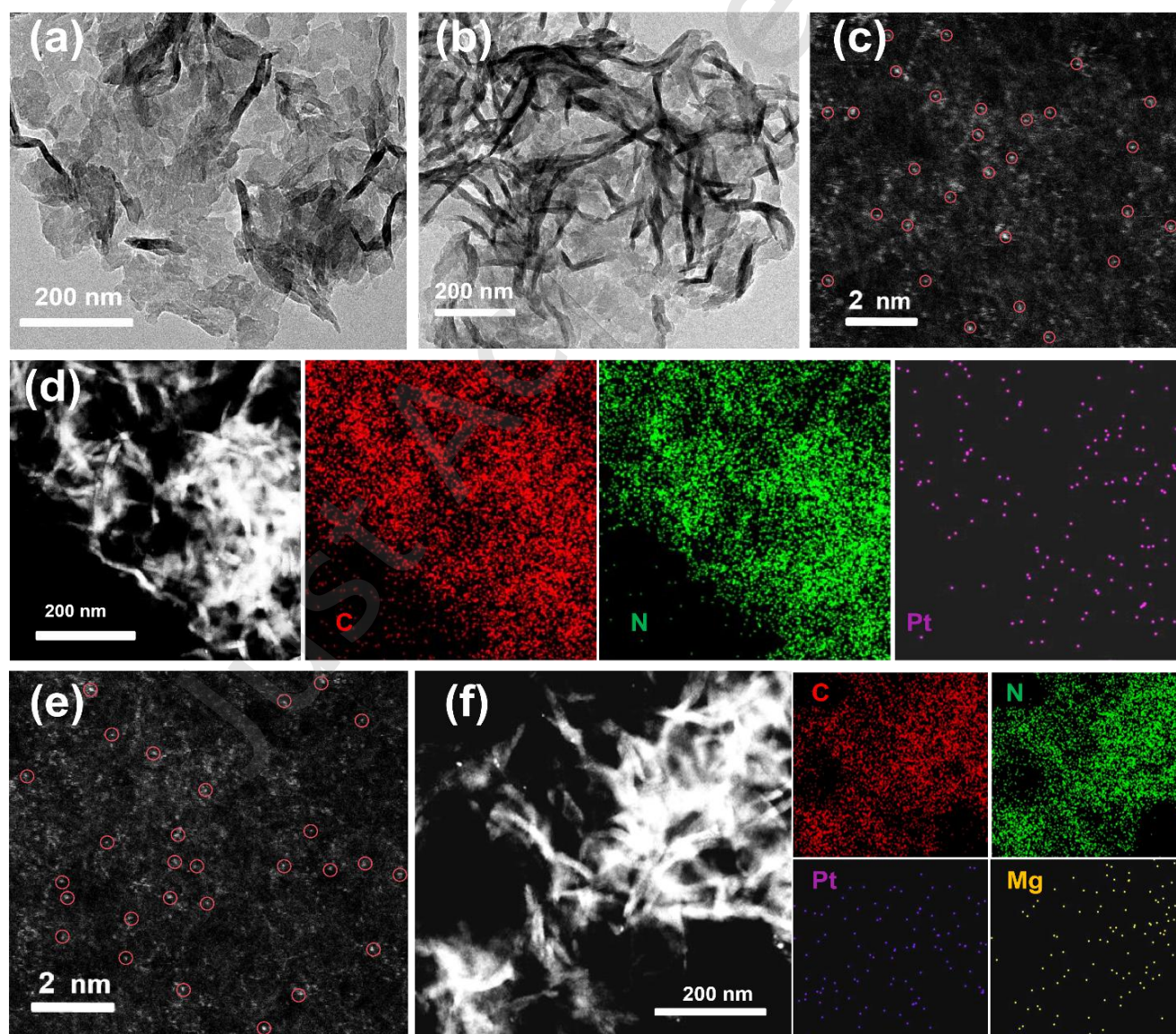


Figure 1 (a) TEM image of Pt-CN. (b) TEM image of MgPt-CN. (c) AC HAADF-STEM image of Pt-CN. (d) Elemental mappings of Pt-CN. (e) AC HAADF-STEM image of MgPt-CN. (f) Elemental mappings of MgPt-CN.

images depicted in Figs. 1(a-b) and Figs. S8(b-d) showed a curly

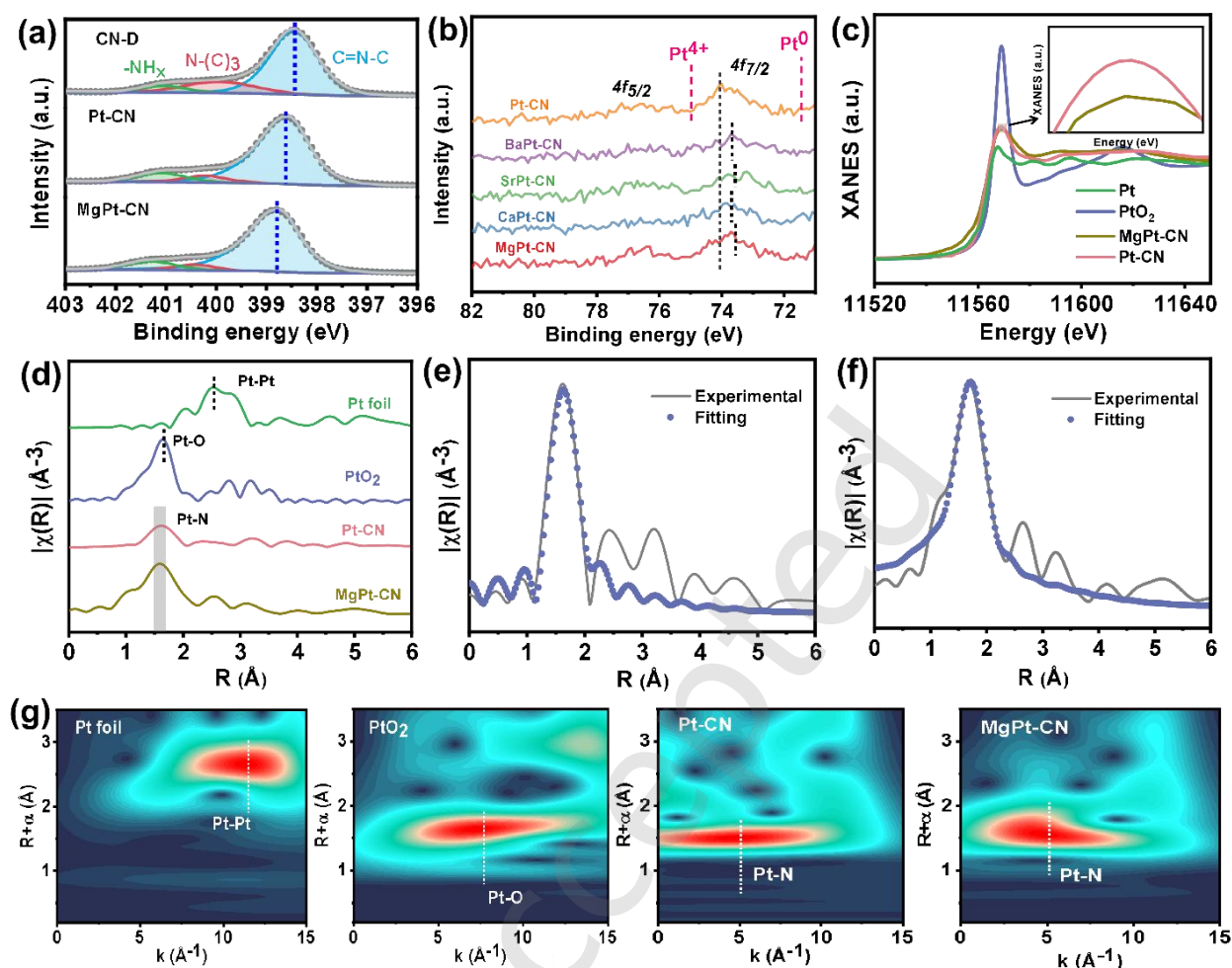


Figure 2 (a) High-resolution XPS spectra of N 1s. (b) High-resolution XPS spectra of Pt 4f. (c) Pt L-edge XANES spectra. (d) Pt L-edge EXAFS spectra in R space for Pt-CN and MgPt-CN. (e) EXAFS R-space fitting curves for Pt-CN. (f) EXAFS R-space fitting curves for MgPt-CN. (g) WT EXAFS spectra of Pt foil, PtO₂, Pt-CN and MgPt-CN.

uniform distribution of Pt, Mg, N and C in MgPt-CN was also verified by EDS elemental mapping analysis (Fig. 1(f)).

X-ray photoelectron spectroscopy (XPS) was performed to determine the chemical compositions and valence states of synthesized samples. As shown in Fig. 2(a), the N 1s XPS spectrum of CN-D exhibited three peaks, located at 398.5, 400.0 and 401.1 eV, which could be attributed to N atoms in C=N=C, N-(C)₃ and -NH_x, respectively [35]. Similarly, the spectra of Pt-CN (Fig. 2(a)) and AMPt-CN (Fig. 2(a) and Fig. S15 in the ESM) contained the same three peaks. Significantly, after loading metal atoms, the peaks assigned to C=N=C (pyridinic N), which could bind to metal atoms as an electron donor and thus increase the number of metal catalytic sites [36], displayed a slight shift to higher-energy side compared to that of pure CN-D in Fig. 2(a) and Fig. S16 in the ESM. This positive shift confirmed a strong coordination interaction between the metal atoms and pyridinic N [37, 38]. Besides, the binding energy of the Pt 4f_{7/2} peak for Pt-CN was approximately 74.0 eV (Fig. 2(b)), located between those of Pt⁰ (71.5 eV) and Pt⁴⁺ (75.0 eV) [39], indicating Pt species exist in an oxidized state as Pt^{δ+} (0<δ<4). Notably, after the addition of alkaline earth metals, there was a negative shift of the Pt 4f_{7/2} XPS peak in contrast to Pt-CN (Fig. 2(b)). This shift was indicative of more electrons

transfer to the Pt centers, demonstrating the electron configuration of Pt single atoms can be effectively regulated via introducing of alkaline earth metals. Subsequently, the valence state of different alkaline earth metals were also studied. The Mg 1s spectrum of MgPt-CN (Fig. S17(a) in the ESM) exhibited a single peak at 1304.2 eV, assigned to Mg-N bonds [40, 41], revealing Mg was probably atomic bonded with nitrogen. Meanwhile, the +2 oxidation state of Mg was confirmed, as its binding energy was closer to that of Mg²⁺ ions (1304 eV) than to that of metallic Mg (1303.5 eV) [40]. In addition, Ca 2p spectrum of CaPt-CN, Sr 3d spectrum of SrPt-CN and Ba 3d spectrum of BaPt-CN, presented in Fig. S17 in the ESM, indicated that the valence states of Ca [42], Sr [43] and Ba [44] were also +2.

X-ray absorption fine structure (XAFS) spectroscopy experiments were conducted to gain more information on the chemical environments. As depicted in X-ray absorption near-edge structure (XANES) spectra (Fig. 2(c)), the white-line intensity of Pt-CN and MgPt-CN was located between that of Pt foil and PtO₂, suggesting the oxidation state of Pt^{δ+} (0 < δ < 4) in both Pt-CN and MgPt-CN. Moreover, the inset of Fig. 2(c) revealed that the white-line intensity of MgPt-CN was weaker than that of Pt-CN, suggesting a lower average valence state of

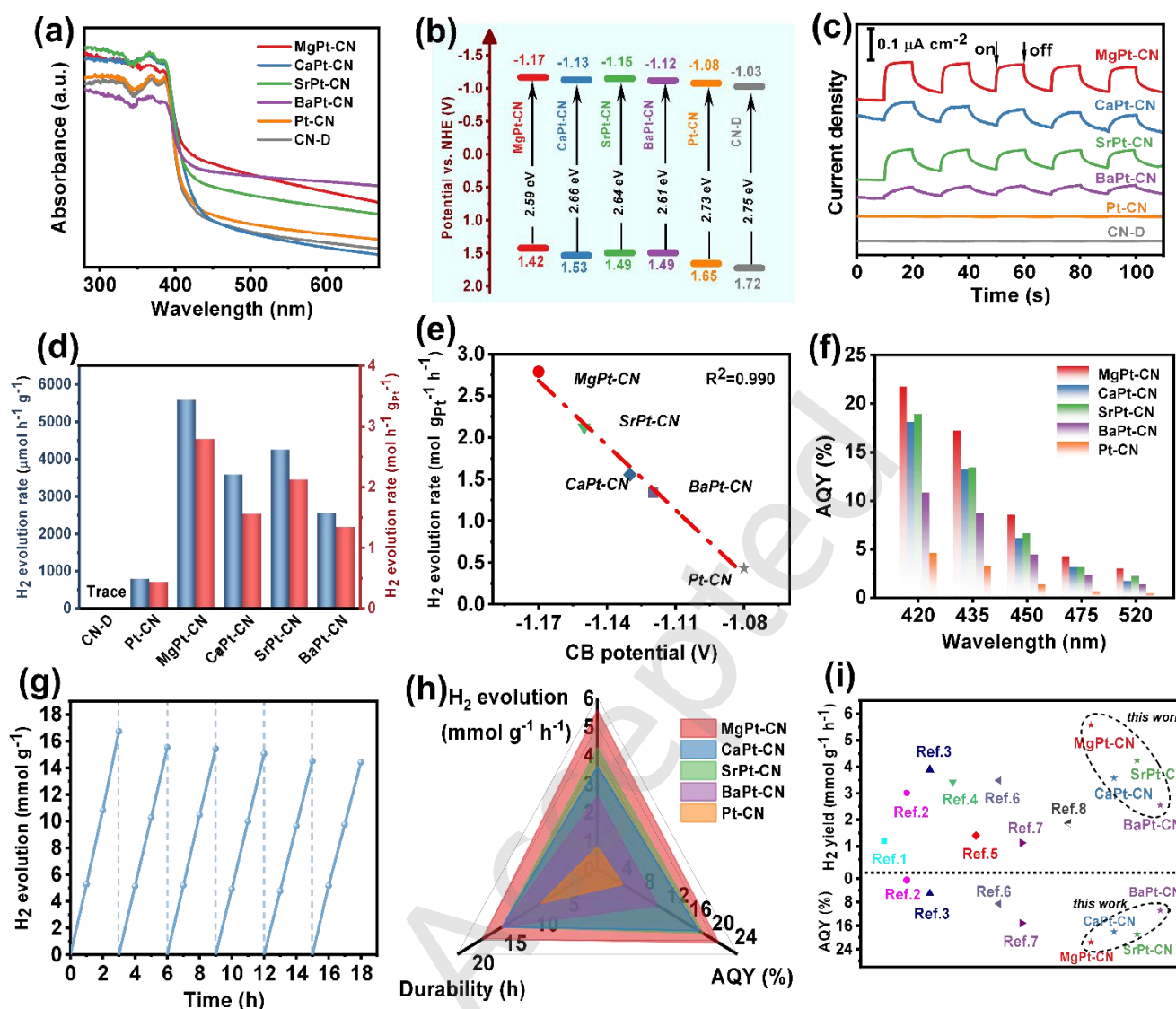


Figure 3 (a) UV-vis diffuse reflectance spectra. (b) Energy band structure. (c) Photocurrent response. (d) Photocatalytic hydrogen evolution activities. (e) Linear relationships between the activities of AMPt-CN and CB potential. (f) AQY for photocatalytic H₂ evolution. (g) Cycling hydrogen evolution activity of MgPt-CN. (h) Comparison of AMPt-CN with Pt-CN in H₂ evolution, durability and AQY. (i) H₂ evolution and AQY comparison with related Pt SACs from previous reports (Table S3 in the ESM).

Pt in MgPt-CN. This observation was in good agreement with the XPS results (Fig. 2(b)) and further implied the valence state of Pt was modulated by alkaline earth metals. The corresponding Fourier-transform extended X-ray absorption fine structure (FT-EXAFS) spectra for Pt-CN and MgPt-CN were presented in Fig. 2(d). The scattering oscillations of Pt-CN and MgPt-CN were distinctly different from that of Pt foil. Specifically, the dominant peak at approximately 1.61 Å was associated with Pt-N bonding, while the peak near 2.54 Å, characteristic of Pt-Pt metallic bonds, was absent, proving the presence of atomic Pt sites in Pt-CN and MgPt-CN [45, 46]. Furthermore, based on the fitting results (Figs. 2(e-f) and Table S2 in the ESM), both Pt-CN and MgPt-CN were equipped with Pt-N₂ coordination. The wavelet transform-EXAFS (WT-EXAFS) spectrum of Pt-CN and MgPt-CN (Fig. 2(g)) exhibited a prominent peak centered at $k \sim 5.1 \text{ Å}^{-1}$ related to the Pt-N coordination and were different from the signals of Pt foil and PtO₂. This distinction provided further evidence for the atomic dispersion of Pt sites in both Pt-CN and MgPt-CN samples. In summary, Pt was atomically

dispersed in Pt-CN and MgPt-CN, and the introduction of alkaline earth metals did not significantly alter the local coordination structure of the Pt atoms but effectively modulated their chemical valence.

UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was used to investigate the optical absorption properties of the prepared samples. The AMPt-CN samples showed an enhanced absorption edge with a slight redshift compared to Pt-CN and pure CN-D (Fig. 3(a)), which meant introducing alkaline earth metal sites improved their visible-light absorption. The band gaps of the samples were estimated from the Tauc plots (Fig. S18 in the ESM) using the Kubelka-Munk transformation [47, 48]. The calculated band gaps of CN-D, Pt-CN, MgPt-CN, CaPt-CN, SrPt-CN and BaPt-CN were 2.75, 2.73, 2.59, 2.66, 2.64 and 2.61 eV, respectively. Mott-Schottky plots in Fig. S19 revealed positive slopes for all synthesized samples, confirming their n-type semiconductor characteristics. The corresponding flat band potentials of CN-D, Pt-CN, MgPt-CN, CaPt-CN, SrPt-CN and BaPt-CN were estimated to be -1.03, -1.08, -1.17, -1.13,

-1.15 and -1.12 V (vs. NHE), respectively. It is accepted that the conduction band (CB) potential is approximately equal to the flat band potential in n-type semiconductor [49]. Accordingly, the corresponding energy band structure was depicted in Fig. 3(b). Evidently, the AMPt-CN samples possessed more negative conduction band potentials than Pt-CN and it was deemed to be more favorable for proton reduction. Besides, the narrower band gap facilitated visible-light absorption [50], collectively contributing to the superior photocatalytic performance.

The separation and transfer behavior of photogenerated charge carriers were investigated by photoluminescence (PL) spectroscopy, transient photocurrent response, linear sweep voltammetry (LSV) plots and electrochemical impedance spectroscopy (EIS) curves. The dramatically quenched PL emission intensity of the AMPt-CN samples (Fig. S20 in the ESM) signified the suppressed recombination of electrons and holes. The photocurrent intensity of AMPt-CN climbed apparently compared to that of CN-D and Pt-CN (Fig. 3(c)), reflecting that charge transfer ability was promoted effectively after modification with alkaline earth metals. Moreover, combining with alkaline earth metals contributed to higher current density in the LSV plots (Fig. S21 in the ESM), showing a faster migration rate of charge carriers [51, 52]. Both the transient photocurrent responses and LSV tests directly demonstrated that AMPt-CN samples achieved more efficient charge separation and provided a larger population of photogenerated electrons for the reduction reaction, outperforming Pt-CN. Meanwhile, as displayed in Fig. S22 in the ESM, the radii of the Nyquist plots followed a trend of $R(\text{MgPt-CN}) < R(\text{SrPt-CN}) < R(\text{CaPt-CN}) < R(\text{BaPt-CN}) < R(\text{Pt-CN}) < R(\text{CN-D})$. This trend revealed the existence of alkaline earth metals favored the electrical conductivity and reduced charge transfer resistance. Collectively, these optical and electrochemical measurements certified the enhanced separation and migration of photoinduced charge carriers after doping with alkaline earth metals, suggesting a superior hydrogen evolution capability for AMPt-CN catalysts.

The photocatalytic hydrogen evolution reaction performance was evaluated under visible-light irradiation ($\lambda > 420$ nm). As shown in Fig. S23 in the ESM, alkaline earth metals doped

samples exhibited much higher H_2 production than Pt-CN. In Fig. 3(d), CN-D showed only a trace amount of H_2 evolution. After loading Pt sites, the photocatalytic H_2 evolution rate of Pt-CN was improved to $779 \mu\text{mol g}^{-1} \text{h}^{-1}$, indicating that Pt served as an effective active site for the reaction. After anchoring alkaline earth metals, the H_2 production rates of MgPt-CN, CaPt-CN, SrPt-CN and BaPt-CN were greatly increased to 5578, 3574, 4243 and $2550 \mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. These values are 7.2, 4.6, 5.4, and 3.3 times higher than that of Pt-CN, respectively. Notably, the activity trend was not strictly correlated with the electronegativity of alkaline earth metals, suggesting that the promotional effect was determined by multiple factors, including AM loading, N-AM coordination model and strength, structural compatibility with the $\text{g-C}_3\text{N}_4$ cavity and other related factors. Combined with the ICP results (Table S1 in the ESM), the Pt mass-specific H_2 production rates of the catalysts were expressed as follows: $0.43 \text{ mol g}_{\text{Pt}}^{-1} \text{h}^{-1}$ (Pt-CN), $2.79 \text{ mol g}_{\text{Pt}}^{-1} \text{h}^{-1}$ (MgPt-CN), $1.55 \text{ mol g}_{\text{Pt}}^{-1} \text{h}^{-1}$ (CaPt-CN), $2.12 \text{ mol g}_{\text{Pt}}^{-1} \text{h}^{-1}$ (SrPt-CN), and $1.34 \text{ mol g}_{\text{Pt}}^{-1} \text{h}^{-1}$ (BaPt-CN). Linear regression analysis yielded an R^2 value of 0.990, suggesting a strong linear correlation between the H_2 evolution rate and CB potential (Fig. 3(e)). Notably, the H_2 yields of Mg-CN, Ca-CN, Sr-CN and Ba-CN without Pt sites were only 25.5, 22.6, 12.0 and $17.0 \mu\text{mol g}^{-1} \text{h}^{-1}$, respectively (Fig. S24 in the ESM). This result confirmed individual alkaline earth were not responsible for the advance of H_2 evolution rate and declared the synergistic effect of alkaline earth metal and Pt sites was accounted for H_2 yield enhancement. More importantly, the incorporation of alkaline earth metals also led to a remarkable increase in the apparent quantum yield (AQY) (Fig. 3(f)). Compared to Pt-CN, the AMPt-CN catalysts exhibited significantly higher AQYs across the wavelength range of 420 to 520 nm. Specifically, the AQY at 420 nm reached 21.7% for MgPt-CN, 18.1% for CaPt-CN, 18.9% for SrPt-CN, and 10.8% for BaPt-CN, respectively. These high AQY values meant more photons were absorbed and more photo-induced electrons were utilized for photocatalytic H_2 evolution. Furthermore, the

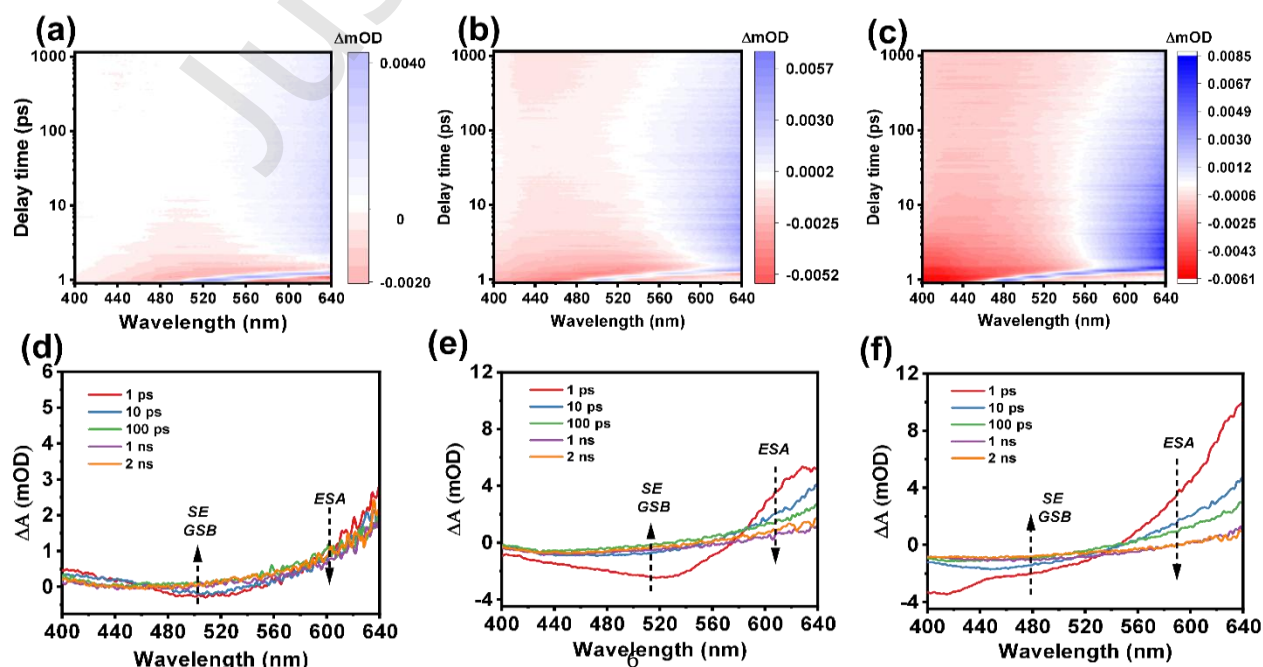


Figure 4 2D mapping fs-TA (pump laser: 350 nm) of (a) CN-D, (b) Pt-CN and (c) MgPt-CN; fs-TAS spectra of (d) CN-D, (e) Pt-CN and (f) MgPt-CN.

stability and durability of photocatalysts were assessed by cycling tests. Figure S25(a) in the ESM illustrated the hydrogen production activity of Pt-CN declined distinctly after three cycles. In contrast, the coupling of alkaline earth metals could enhance the stability and durability of Pt SACs (Fig. 3(h) and Figs. S25(b-d) in the ESM). Especially, as displayed in Fig. 3(g), MgPt-CN maintained superior catalytic activity over six consecutive cycles. In addition, the SEM and XRD analysis confirmed no evident alterations in the crystallinity and microstructure of MgPt-CN, CaPt-CN, SrPt-CN and BaPt-CN after cycling test (Figs. S26 and S27 in the ESM). And the TEM and AC HAADF-STEM of MgPt-CN after cycling test (Fig. S27 in the ESM) showed no obvious nanoparticles or clusters. These results verified the structural stability and single atom stability of MgPt-CN during photocatalytic H₂ evolution. As visually summarized in Fig. 3h, the AMPt-CN catalysts exhibited substantial improvements in H₂ evolution rate, durability and AQY compared to Pt-CN. Notably, the hydrogen production activity and AQY of the AMPt-CN catalysts, particularly MgPt-CN, surpassed those of most previously reported Pt-based single-atom catalysts (Fig. 3(i) and Table S3 in the ESM). These collective findings underscored the crucial role of alkaline earth metals in enhancing photocatalytic performance of Pt SACs.

Femtosecond transient absorption spectroscopy (fs-TAS, excited by 350 nm laser) was carried out to gain further insight into the effect of alkaline earth metals. As observed in Figs. 4(a-c), CN-D, Pt-CN and MgPt-CN all showed a broad negative absorption feature from approximately 440 to 560 nm and a positive absorption feature from approximately 560 to 640 nm. This negative feature, resulting from the ground state bleaching (GSB) or stimulated emission (SE), was related to the recombination of electron-hole pairs [53]. The positive signal, assigned to excited-state absorption (ESA), was caused by surface-trapped photogenerated electrons or electron-hole pairs [54]. Compared to CN-D (Fig. 4(d)), both Pt-CN (Fig. 4(e)) and MgPt-CN (Fig. 4(f)) displayed markedly enhanced TAS signal intensities, suggesting an increased population of photogenerated electrons [55]. Note that MgPt-CN (Fig. 4(f)) exhibited a weaker negative signal (GSB or SE) and a stronger positive signal (ESA) than Pt-CN (Fig. 4(e)). Together with the PL, photocurrent and LSV results, these TAS results supported the recombination of photogenerated electrons and holes was suppressed and the charge separation was boosted after modification with alkaline earth metals. The ESA kinetics was further analyzed by fitting the decay profile at 620 nm. In Fig. S28 in the ESM, the decay kinetics of CN-D was fitted with two time constants of 2.1 ps and 188.6 ps, which were attributed to the undesirable photogenerated electron-hole recombination (τ_1) and the shallow charge capture (τ_2) [55, 56], respectively. For Pt-CN and MgPt-CN, the fitted lifetimes were $\tau_1 = 11.1$ ps and $\tau_2 = 238.1$ ps for Pt-CN, and $\tau_1 = 24.5$ ps and $\tau_2 = 287.0$ ps for MgPt-CN (Fig. S28 in the ESM). The prolonged lifetime of τ_1 was the result of efficient utilization of the photo-excited electrons and slower decay of τ_2 derived from enhanced active electron mobility for the photocatalytic H₂ evolution. From the above results, the pivotal function of alkaline earth metal towards high AQY and outstanding photocatalytic performance can be well elucidated.

DFT calculations were employed to further unravel the significant role of alkaline earth metals. Computational models

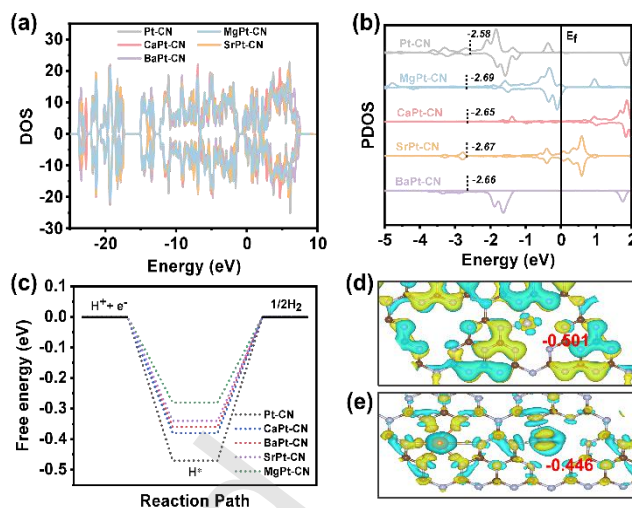


Figure 5 (a) DOS plots of AMPt-CN. (b) PDOS plots of Pt 5d orbitals and the corresponding d-band center positions (black dashed line). (c) Calculated Gibbs free energy diagrams of H₂ evolution reaction. Differential charge density and Bader charge of Pt over (d) Pt-CN and (e) MgPt-CN.

of Pt-CN and the four AMPt-CN catalysts were constructed in Fig. S29 in the ESM. As displayed in Fig. 5(a) and 5(b), the existence of alkaline earth metals caused only minor differences in the total density of states (DOS), but induced an apparent variation in the partial density of states (PDOS) of Pt 5d orbitals, indicating the charge exchange interaction between alkaline earth metals and Pt. Impressively, relative to Pt-CN, the d-band centers of Pt in AMPt-CN samples shifted away from Fermi energy level (Fig. 5(b)). This downward shift of d-band center could pull more antibonding states below the Fermi level, weaken the H* binding and facilitate the desorption of H* [57, 58], which was conducive to the formation of H₂. In addition, the absolute value of free energy (ΔG_{H^*}) is a critical descriptor for evaluating the HER activity of photocatalysts. Notably, the ΔG_{H^*} of Pt-CN was calculated to be -0.47 eV in Fig. 5(c). In contrast, all AMPt-CN samples possessed a more positive ΔG_{H^*} (-0.28 eV for MgPt-CN, -0.34 eV for SrPt-CN, -0.36 eV for BaPt-CN and -0.38 eV for CaPt-CN). This trend indicated modifying Pt-CN with alkaline earth metals can effectively reduce the free energy barrier of HER, thereby accelerating the kinetics of hydrogen evolution [59]. The differential charge density was analyzed to explore charge distribution of Pt atoms. In the corresponding plots (Figs. 5(d) and 5(e), Fig. S30 in the ESM), yellow and cyan regions represented charge accumulation and depletion, respectively. The results suggested that the charge density around Pt atoms increased after the introduction of alkaline earth metals. Consistent with this observation, Bader charge analysis indicated an overall increase in the electron density of Pt atom. This finding is demonstrated by the reduction of electron deficiency in Pt, where the Bader charge increased from -0.501 in Pt-CN to a less negative value of -0.446 in MgPt-CN (Figs. 5(d) and 5(e)). The observed positive shift implied that more charge was transferred to the Pt atom. Such electron enrichment at the Pt site was conducive to electron aggregation and promoted the HER [23]. Subsequently, Figure S31 in the ESM exhibited that the work function of AMPt-CN (located between 3.682 and 3.698 eV) was lower than

that of Pt-CN (3.939 eV), which was in favorable for lowering energy barrier for electron emission and facilitating the photocatalytic reaction [60]. Overall, DFT calculations clearly demonstrated the advantages in terms of energy and charge distribution for hydrogen evolution reaction on Pt atom after doping alkaline earth metals.

4 Conclusions

In summary, alkaline earth metals doped AMPt-CN (AM: Mg, Ca, Sr, Ba) catalysts were constructed for enhancing the photocatalytic hydrogen evolution performance of Pt SACs. The incorporation of alkaline earth metals effectively promoted electron transfer from AM to Pt atoms, which played a significant role in optimizing the electronic structure of Pt sites, modulating H* intermediate binding and lowering energy barrier for the hydrogen evolution reaction, meanwhile, also leading to the improved light absorption and enhanced charge separation. As a consequence, compared to Pt-CN, AMPt-CN catalysts exhibited significantly enhanced photocatalytic H₂ production rates with 7.2-, 4.6-, 5.4-, and 3.3-fold improvements for MgPt-CN, CaPt-CN, SrPt-CN, and BaPt-CN, respectively. The corresponding AQYs of AM doped catalysts at 420 nm increased to 21.7%, 18.1%, 18.9%, and 10.8%. Notably, the best performance of MgPt-CN may originate from the smaller ionic radius of Mg, which may allow better structural matching with the g-C₃N₄ cavity and stronger interactions with surrounding N atoms. This facilitated more effective electronic modulation and promoted charge redistribution around Pt sites. Moreover, alkaline earth metals doping elevated conduction band positions of catalysts, and the Pt mass-specific H₂ production rates were linearly related to the corresponding conduction band potentials of Pt-CN, BaPt-CN, CaPt-CN, SrPt-CN and MgPt-CN. Our findings uncovered the pivotal function of alkaline earth metals in adjusting electronic property of Pt SACs and provided a general design principle for efficient photocatalytic hydrogen evolution.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908980>.

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.

Acknowledgements

The present study is supported by the National Natural Science Foundation of China (Nos. 21671176, Nos. 21541011) and Natural Science Foundation of Henan (232300421361). The authors thank the Advanced Analysis & Gene Sequencing Center of Zhengzhou University for assistance in characterization testing.

Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

X. L.: Data curation, project administration, validation, writing manuscript, visualization, software and methodology. Q. H. D.:

visualization and methodology. Y. J. W.: Investigation and visualization. K. W.: software and visualization. Y. K. L.: Conceptualization, project administration and funding acquisition. Z. J. L.: Conceptualization, project administration and funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

None.

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Electronic Supplementary Material

Alkaline earth metals induced electron transfer to Pt single-atom on carbon nitride toward boosting photocatalytic H₂ production

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Supporting information to <https://doi.org/10.26599/NR.2026.94908980>

Characterization

The powder X-ray diffraction (XRD) patterns were collected on a Smartlab SE instrument using Cu K α radiation. The morphology and microstructure of the samples were characterized via Scanning Electron Microscope (SEM, Sigma500) and Transmission Electron Microscope (TEM, Tecnai G2 F20S). X-ray photoelectron spectroscopy (XPS) profiles of the studied materials were acquired using a Thermo Scientific K-Alpha instrument equipped with an Al-K α radiation source. The inductively-coupled plasma optical emission spectrometry (ICP-OES) results were obtained by Agilent 5110. UV-vis DRS and Fourier transform infrared spectra (FTIR) spectra were measured on Cary 5000 spectrophotometer and Scientific Nicolet iS5 spectrometer. The photoluminescence (PL) spectroscopy were measured by Hitachi F-4600. The femtosecond transient absorption spectroscopy (fs-TAS) measurements were collected on a Helios pump-probe system in combination with an amplified femtosecond laser system (Light Conversion CARBIDE-CB5 ORPHEUS). Nitrogen sorption measurements were conducted by gas absorption analyzer (Belsorp Max II). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations were performed using an JEM-ARM200F instrument operating at 200 kV. The X-ray absorption fine structure spectra (Pt L-edge) were collected at 14W 11B beamline in Shanghai Synchrotron Radiation Facility (SSRF). The storage rings of SSRF was operated at 3.5 GeV with a stable current of 200 mA. Using Si(111) double-crystal monochromator, the data collection were carried out in fluorescence mode using Lytle detector. All spectra were collected in ambient conditions.

Theoretical calculations

We used the DFT as implemented in the Vienna Ab initio simulation package (VASP) in all calculations. The exchange-correlation potential is described by using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE). The projector augmented-wave (PAW) method is employed to treat interactions between ion cores and valence electrons. The plane-wave cutoff energy was fixed to 450 eV. Given structural models were relaxed until the Hellmann-Feynman forces smaller than -0.02 eV/Å and the change in energy smaller than 10⁻⁵ eV was attained. The long-range van der Waals interaction is described by the DFT-D3 approach.

The Gibbs free energy change is defined as:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE is the electronic energy calculated with VASP, ΔZPE and ΔS are the zero-point energy difference and the entropy change between the products and reactants, respectively, and T is the temperature (298.15 K).

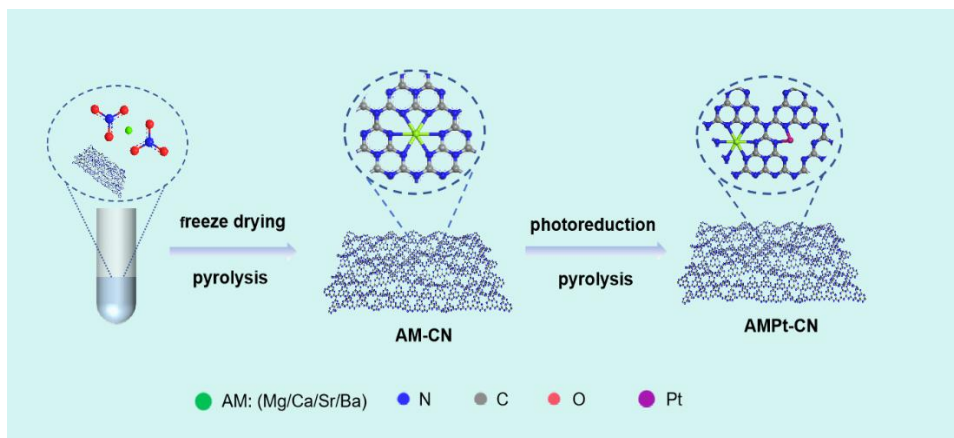


Figure S1 Schematic illustration of the preparation of AMPt-CN.

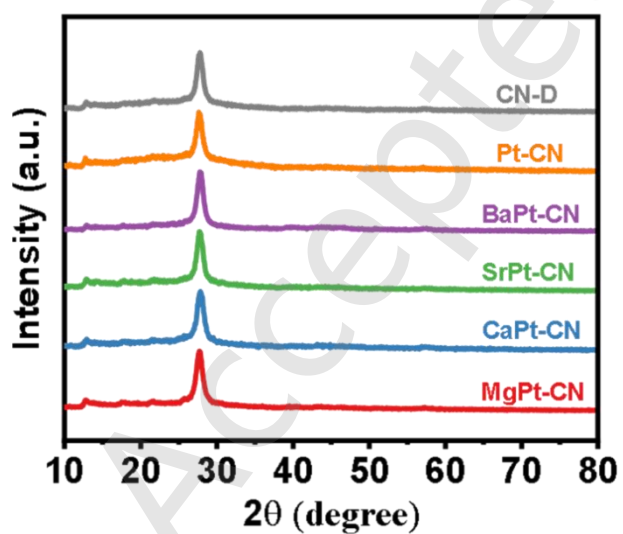


Figure S2 XRD patterns of different samples.

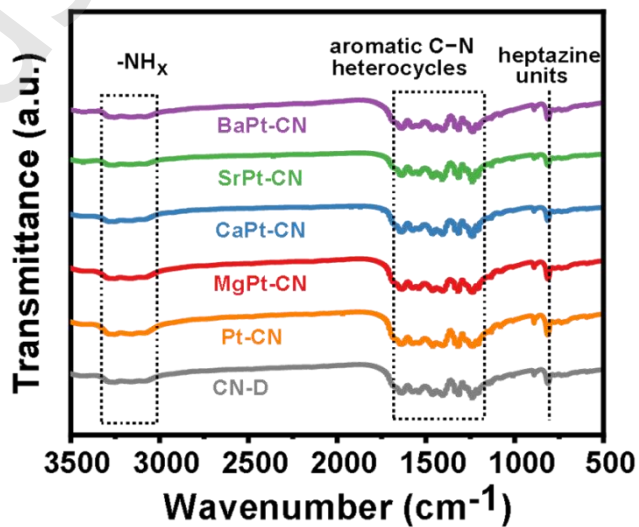


Figure S3 FT-IR spectra of different samples.

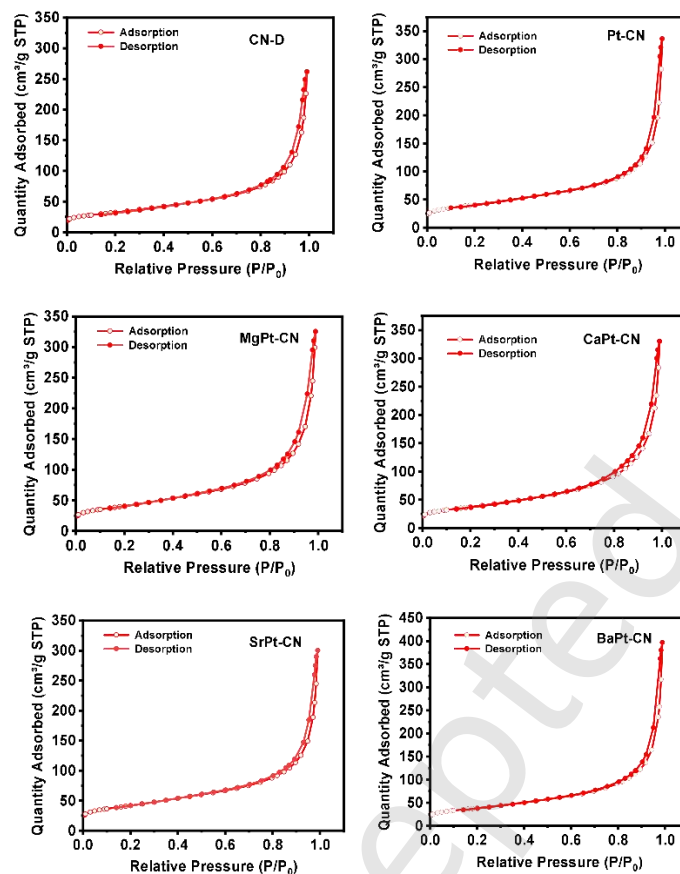


Figure S4 N₂ adsorption-desorption isotherms.

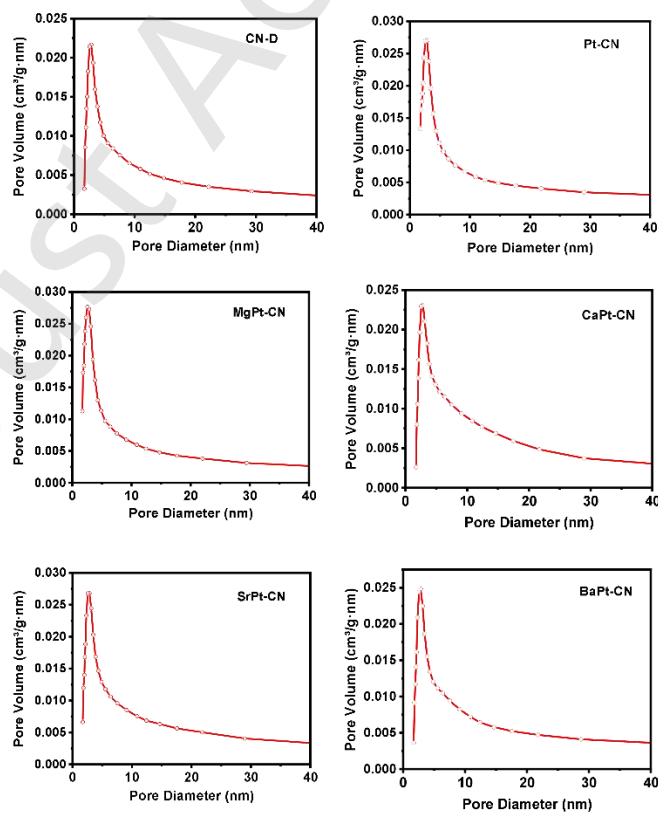


Figure S5 Pore size distribution curves patterns.

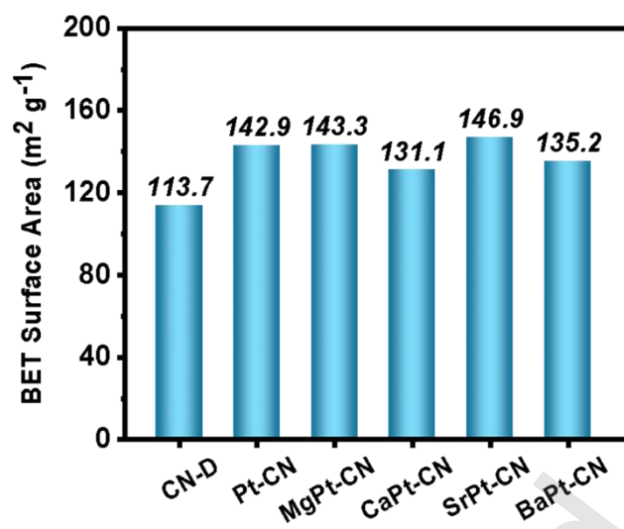


Figure S6 Surface areas derived from BET test.

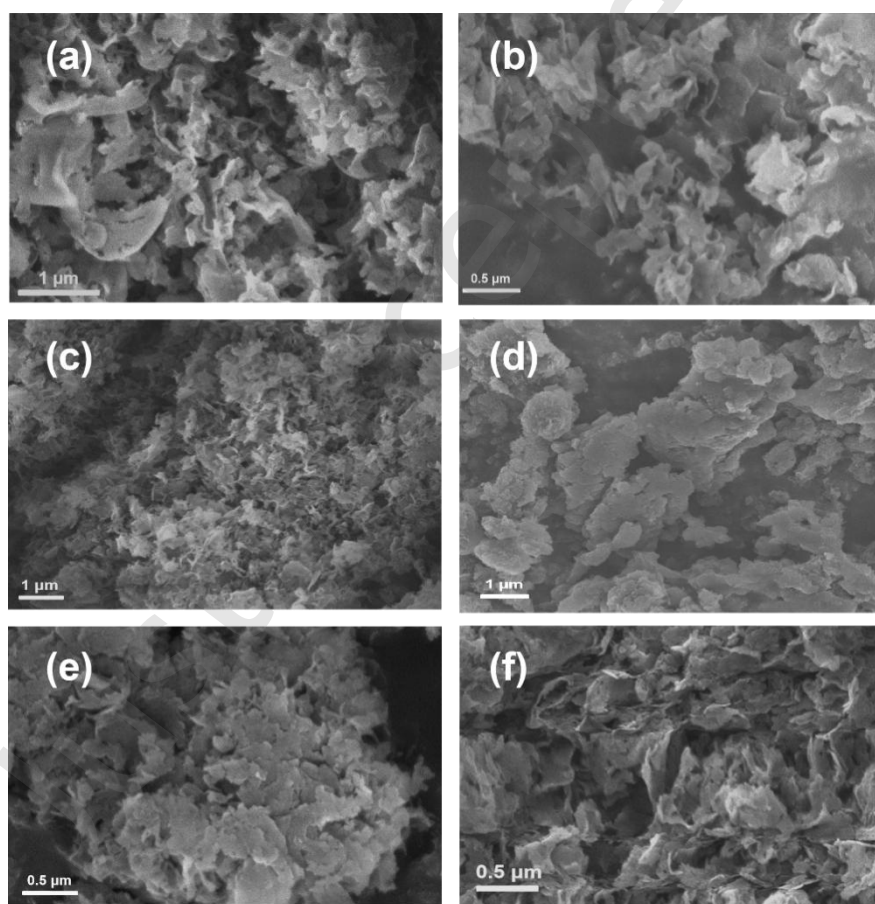


Figure S7 SEM images of (a) CN-D, (b) Pt-CN, (c) MgPt-CN, (d) CaPt-CN, (e) SrPt-CN and (f) BaPt-CN.

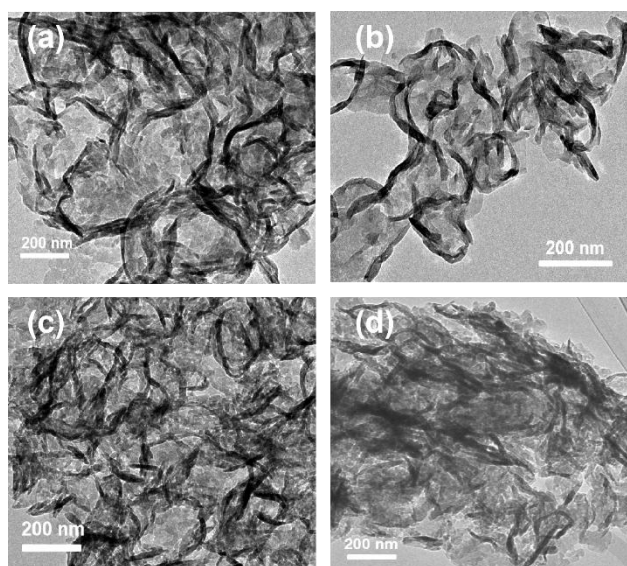


Figure S8 TEM images of (a) CN-D, (b) CaPt-CN, (c) SrPt-CN and (d) BaPt-CN.

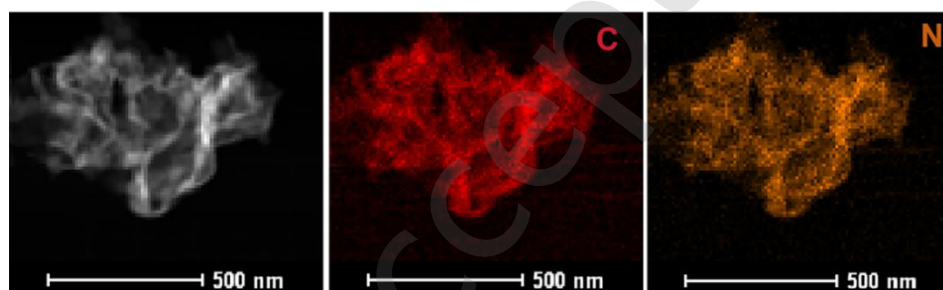


Figure S9 EDS elemental mapping images of CN-D.

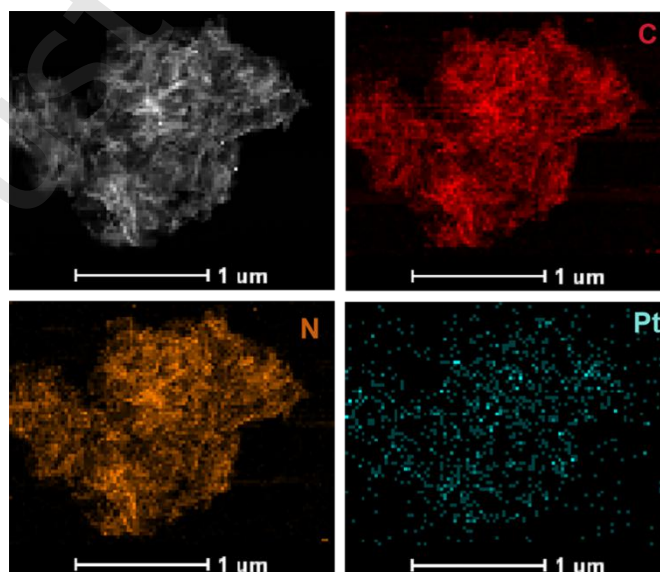


Figure S10 EDS elemental mapping images of Pt-CN.

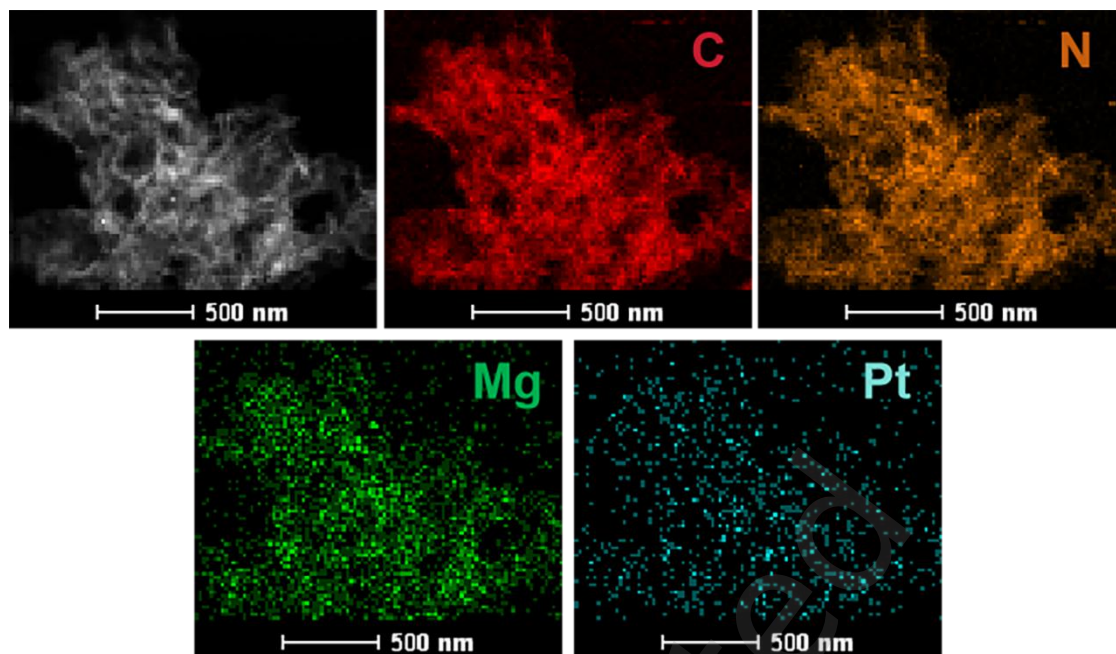


Figure S11 EDS elemental mapping images of MgPt-CN.

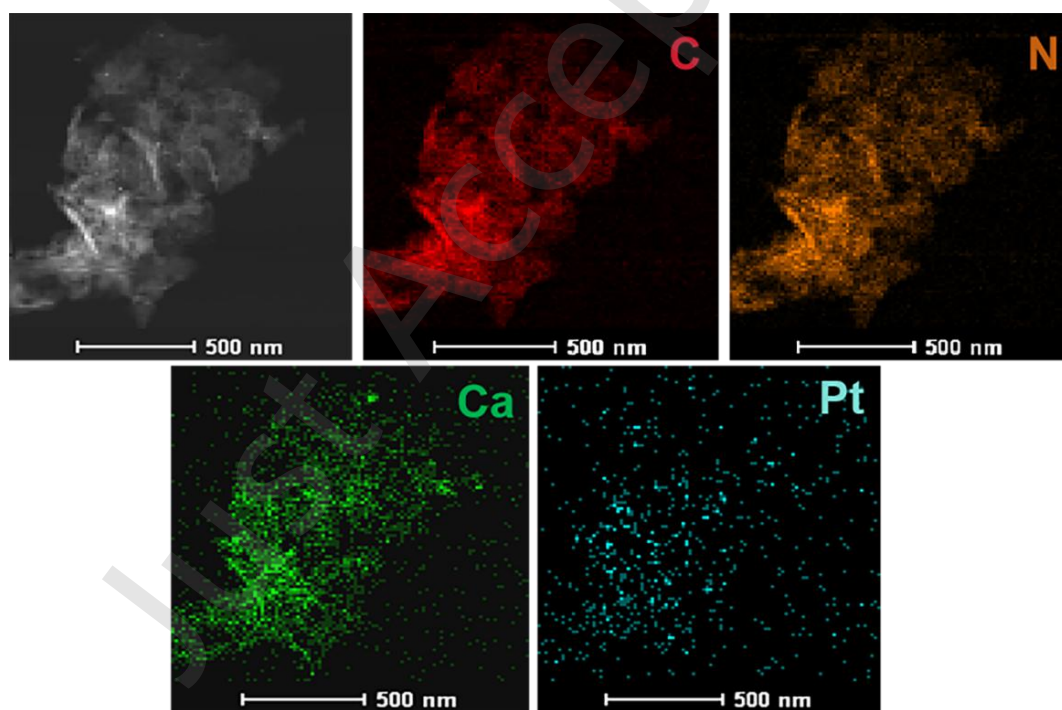


Figure S12 EDS elemental mapping images of CaPt-CN.

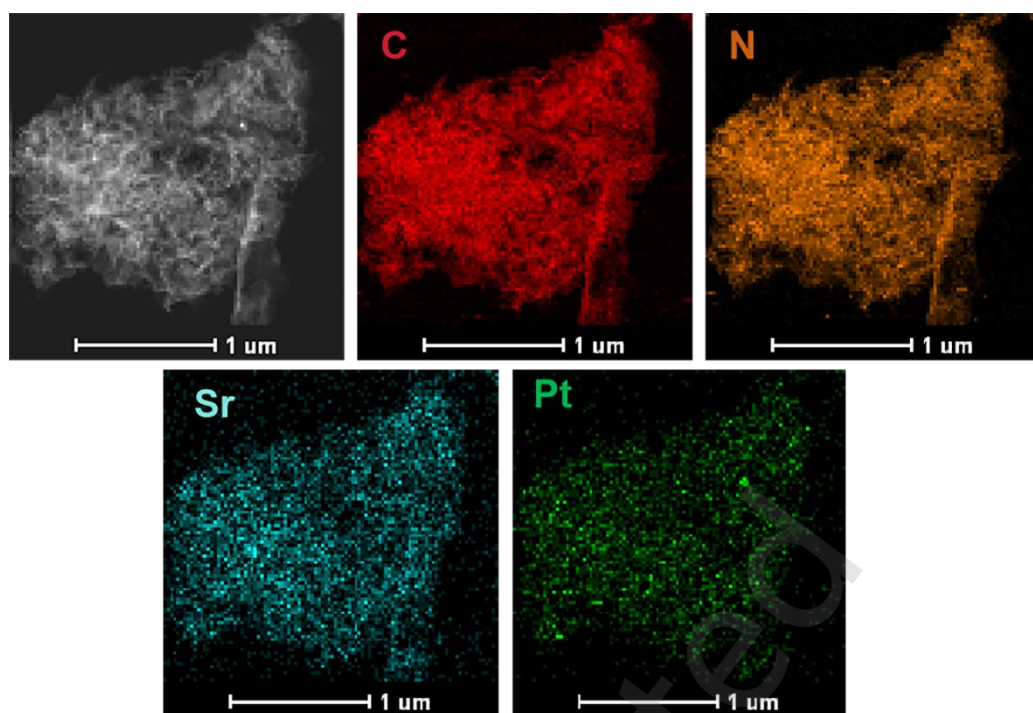


Figure S13 EDS elemental mapping images of SrPt-CN.

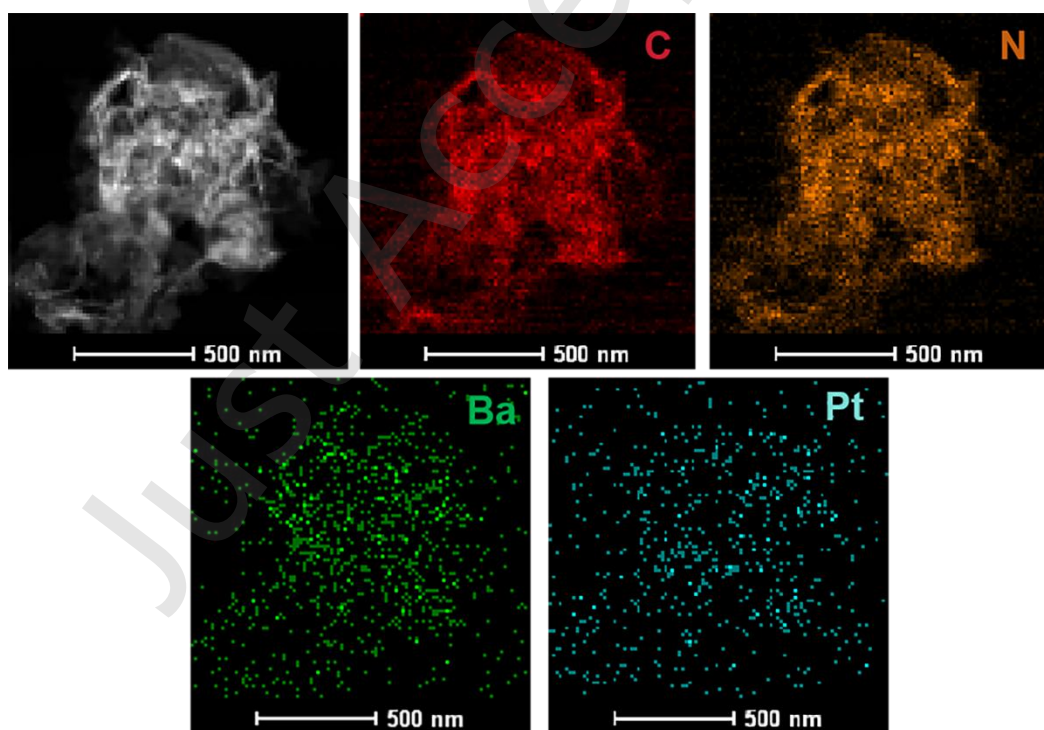


Figure S14 EDS elemental mapping images of BaPt-CN.

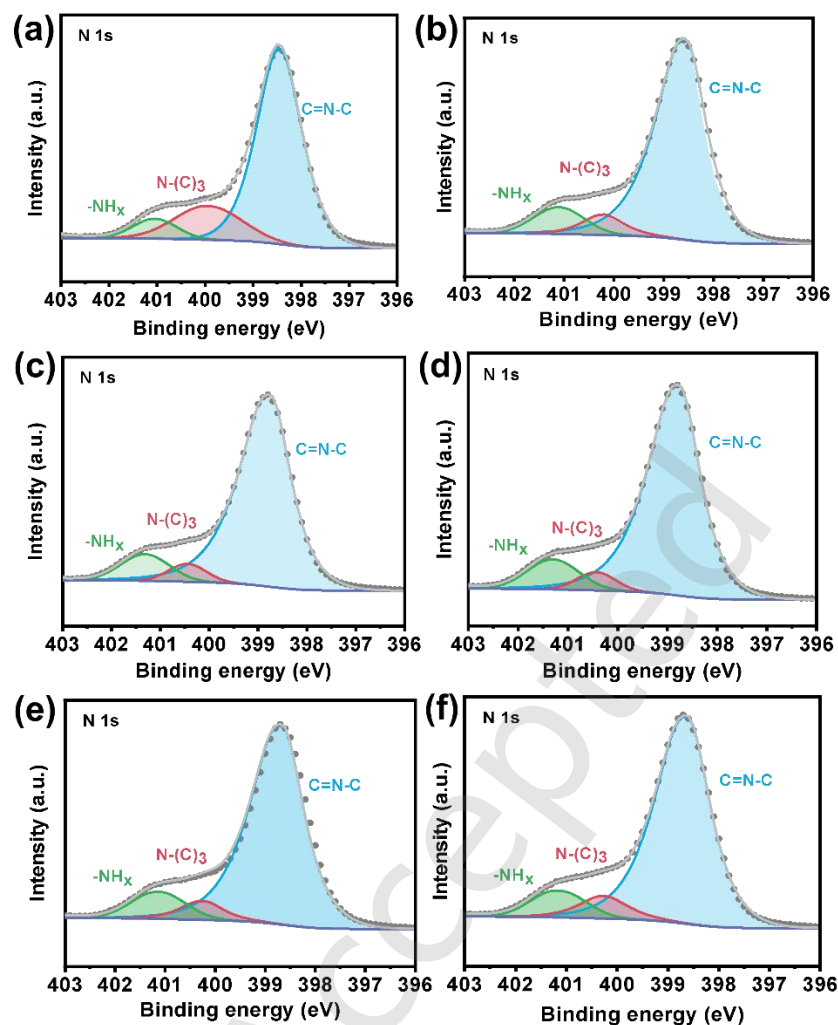


Figure S15 N1s XPS spectra for (a) CN-D, (b) Pt-CN, (c) MgPt-CN, (d) CaPt-CN, (e) SrPt-CN and (f) BaPt-CN.

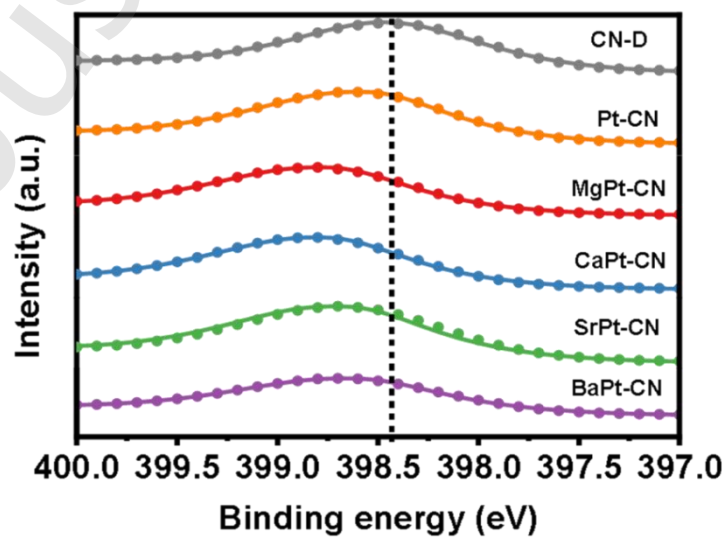


Figure S16 Summary of C-N=C binding energy.

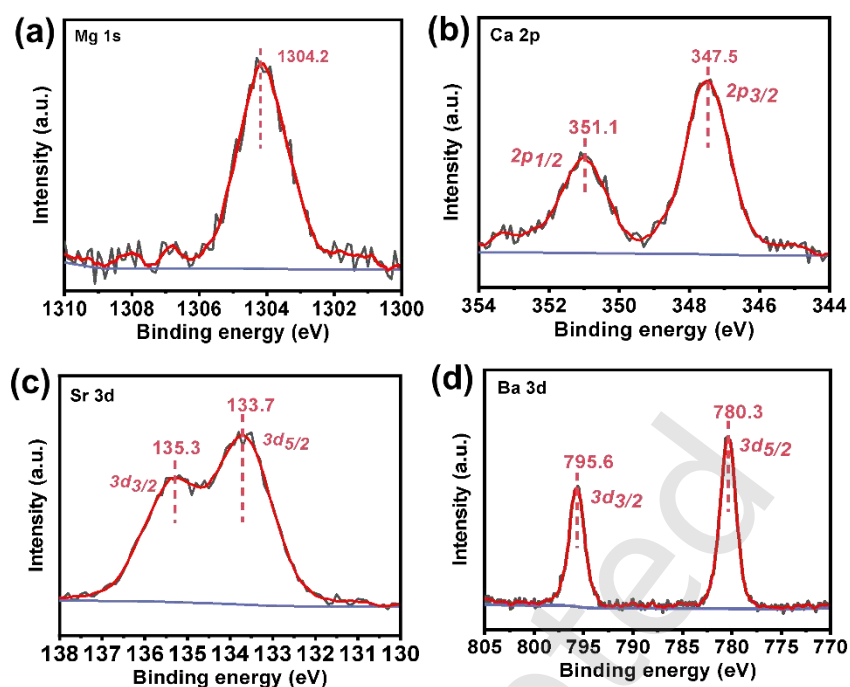
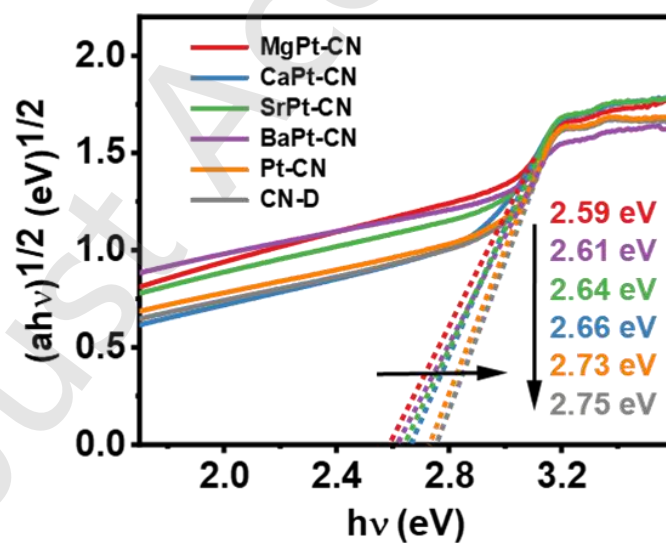
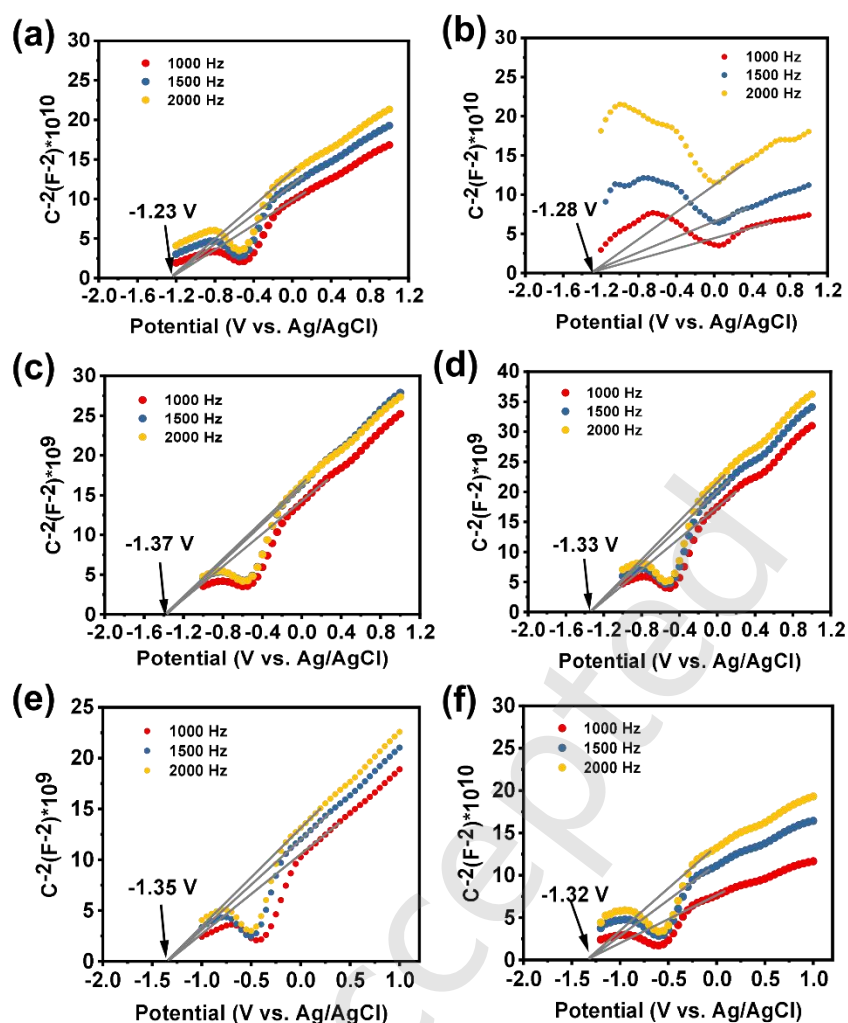


Figure S17 (a) Mg 1s XPS spectrum of MgPt-CN. (b) Ca 2p XPS spectrum of CaPt-CN. (c) Sr 3d XPS spectrum of SrPt-CN. (d) Ba 3d XPS spectrum of BaPt-CN.



Figures S18 Tauc curves.



Figures S19 Mott-Schottky plots of (a) CN-D, (b) Pt-CN, (c) MgPt-CN, (d) CaPt-CN, (e) SrPt-CN and (f) BaPt-CN.

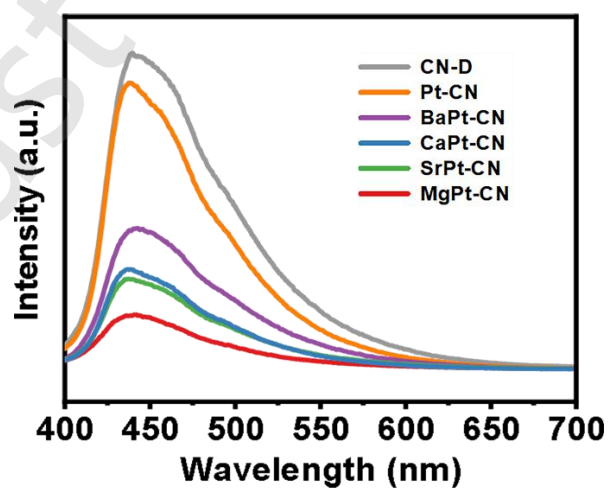


Figure S20 PL spectra.

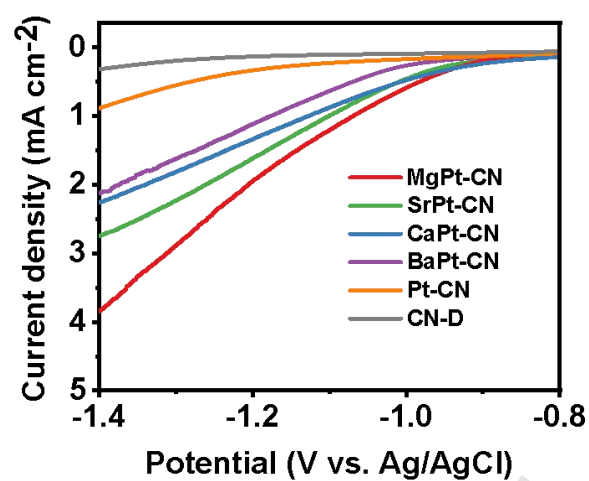


Figure S21 LSV plots.

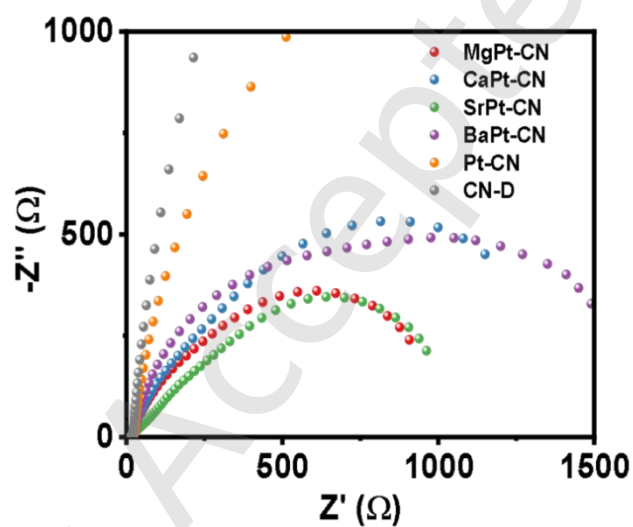


Figure S22 EIS Nyquist plots.

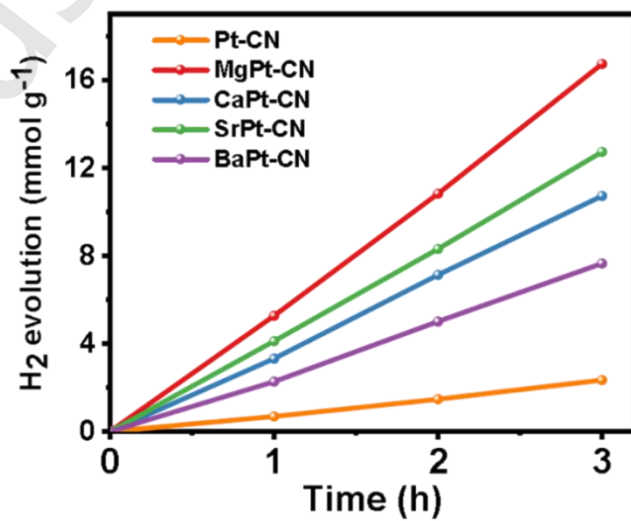


Figure S23 Time course of H_2 production.

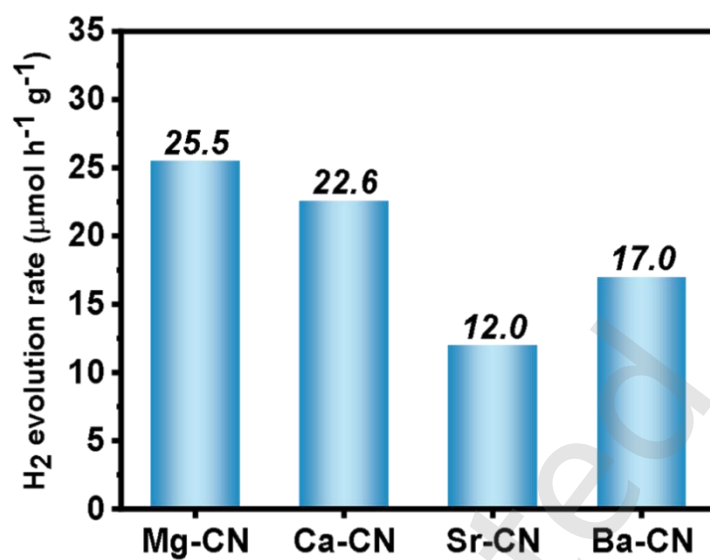


Figure S24 Photocatalytic hydrogen evolution activities of AM-CN.

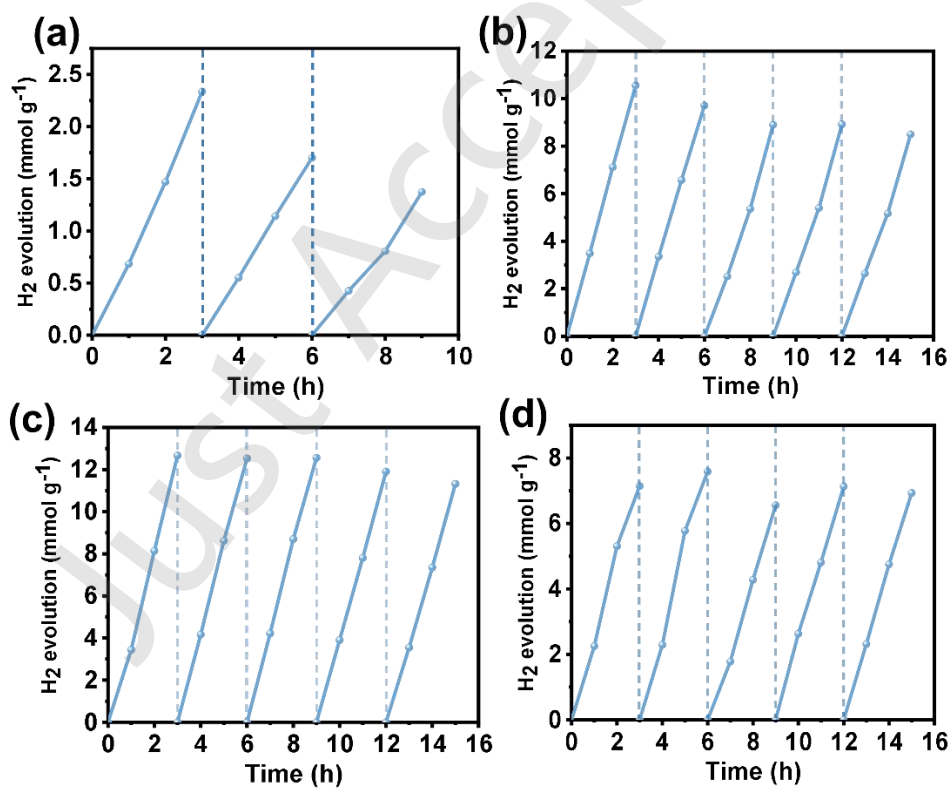


Figure S25 Cycling hydrogen evolution activity of (a) Pt-CN, (b) CaPt-CN, (c) SrPt-CN and (d) BaPt-CN.

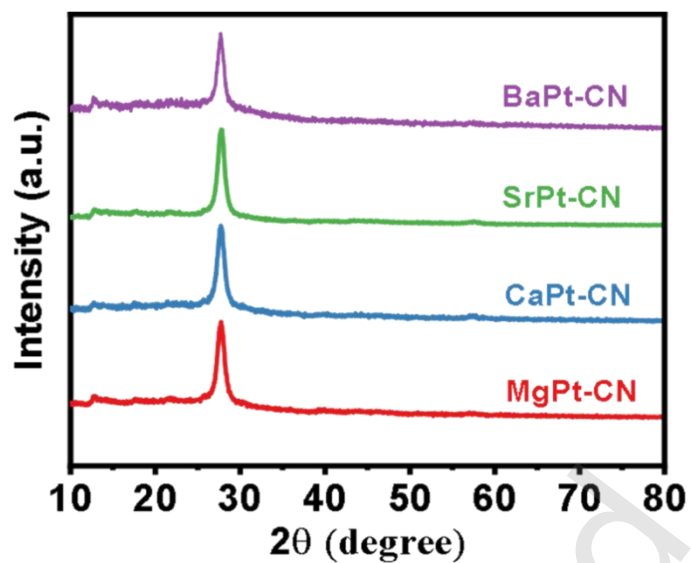


Figure S26 XRD patterns after photocatalytic hydrogen evolution cycling test.

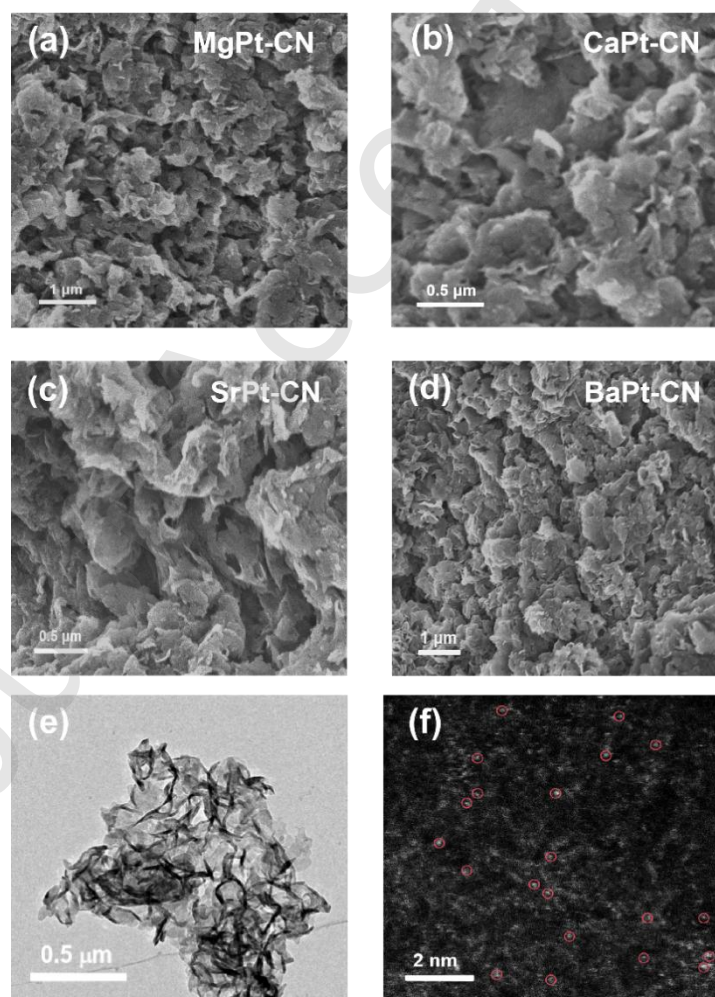


Figure S27 (a-d) SEM images patterns of after photocatalytic hydrogen evolution cycling test. (e) TEM and (f) AC HAADF-STEM of MgPt-CN after photocatalytic hydrogen evolution cycling test.

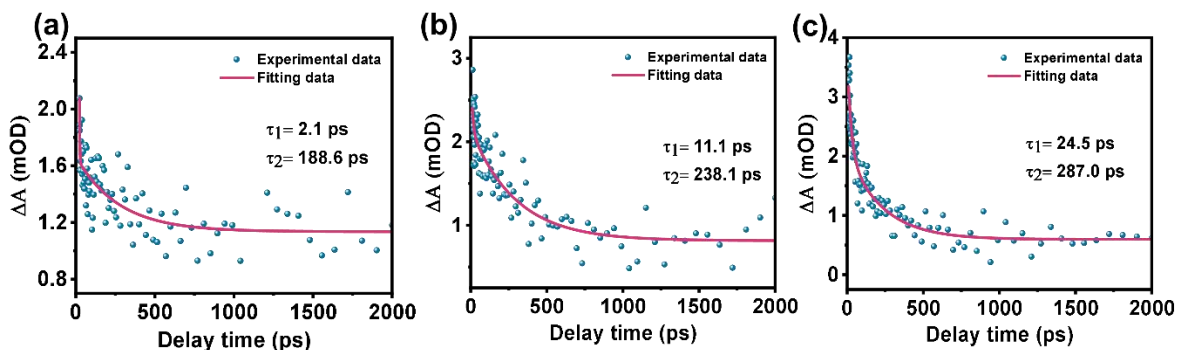


Figure S28 Decay dynamics recorded at 620 nm of (a) CN-D, (b) Pt-CN and (c) MgPt-CN.

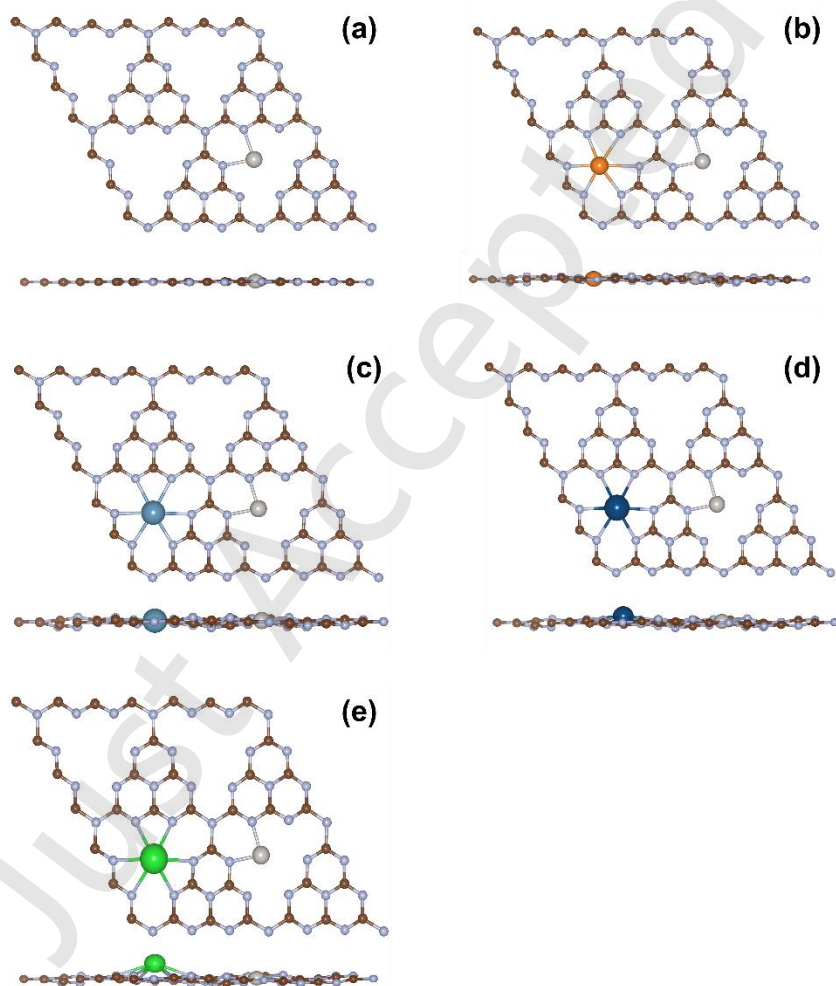


Figure S29 Computational models of (a) Pt-CN, (b) MgPt-CN, (c) CaPt-CN, (d) SrPt-CN and (e) BaPt-CN.

Mg is a light element with a low-energy absorption edge, which provides limited extended oscillations and insufficient data points for Fourier transformation and quantitative fitting [13]. Thus, the precise Mg coordination structure and average coordination number cannot be accurately extracted. And according to previous reports on Mg-modified graphitic carbon nitride [14], Mg species are proposed to be stabilized in the cavity of g-C₃N₄ through coordination with surrounding N atoms. This model was therefore adopted to describe the possible local structure of Mg in MgPt-CN.

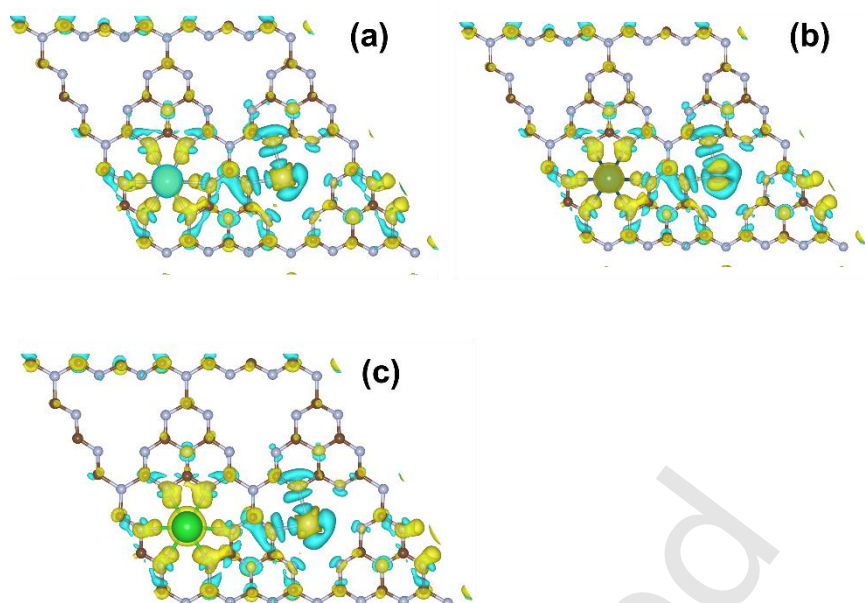


Figure S30 Differential charge density of Pt 5d for (a) CaPt-CN, (b) SrPt-CN and (c) BaPt-CN.

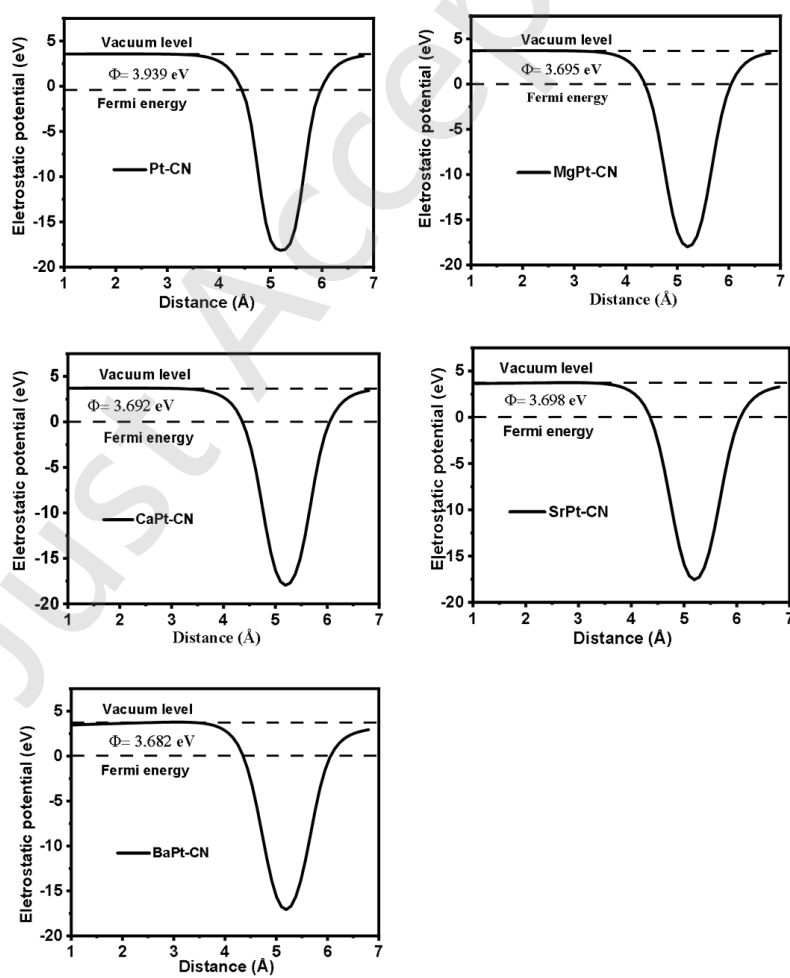


Figure S31 Calculated work function.

Table S1 The metal content of samples obtained from ICP results.

Catalysts	Alkaline earth metal (wt%)	Pt (wt%)
Pt-CN		0.18
MgPt-CN	0.73 (Mg)	0.20
CaPt-CN	2.51 (Ca)	0.23
SrPt-CN	1.94 (Sr)	0.20
BaPt-CN	0.80 (Ba)	0.19

Table S2 Structural parameters extracted from the EXAFS fitting ($S_0^2=0.83$).

sample	shell	CN	R(Å)	$\sigma^2(10^{-3}\text{Å}^2)$	ΔE_0 (eV)	R-factor (%)
Pt foil	Pt-Pt	12	2.77	4.6	5.7	0.2
PtO ₂	Pt-Pt	6	3.13	9.4	8.7	1.3
	Pt-O	6	2.03	3.0		
Pt-CN	Pt-N	1.8	2.02	6.9	7.6	1.9
MgPt-CN	Pt-N	2.1	2.01	7.5	8.3	0.4

CN is the coordination number, R is the average absorber-backscatterer distance, σ^2 is the Debye-Waller factor, ΔE_0 is the inner potential correction and R factor (%) indicates the goodness of fit. The data range used for data fitting in k-space and R-space are 3.0-11.0 Å⁻¹ and 1.0-2.5 Å, respectively. S_0^2 was set to 0.83, according to the experimental EXAFS fit of Pt foil reference.

Table S3 The catalytic performance comparison of previously reported C₃N₄ photocatalysts decorated with Pt single-atoms for hydrogen evolution.

Photocatalysts	Pt (wt%)	H ₂ generationrate (μmol g ⁻¹ h ⁻¹)	AQY (%)	Ref.
Pt _{0.2} -SA-CN	0.11	1219		1
PtSA-CN620	1.72	3020	0.544 (420 nm)	2
PtNv/C ₃ N ₄ (Nv ₆₅₀)	1.0	3,890	5.05 (420 nm)	3
Pt-CN	0.74	3420	0.84 (520 nm)	4
Pt-SA/CN	0.11	1403		5
Pt ₁ Ag ₁ -a/CN	0.21	3480	8.6 (420 nm)	6
V _R -UCN@Pt	2.32	1125	15.2 (420 nm)	7
Pt ₁ -Co ₁ /CN	0.21	1880		8
Pt SAs/C ₃ N ₄	0.91	11472 ^a		9
Pt-MCT-3	1	8600 ^b	27.1 (420 nm)	10
OCN-24	2.68	4091	8.51 (420 nm)	11
SA-Pt-ICN	3.17	18710 ^c	36.9 (420 nm)	12
MgPt-CN	0.20	5578	21.7	this work
CaPt-CN	0.23	3574	18.1	this work
SrPt-CN	0.20	4243	18.9	this work
BaPt-CN	0.19	2550	10.8	this work

* Data on vacancies are not provided in the article.

^a The data were obtained without filter.

^b The reaction temperature is 35 °C.

^c The reaction temperature is 10 °C.

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