

Visible light-regulated Pd single atom catalysts in synergy with Fe atomic clusters for hydrodeoxygenation of vanillin

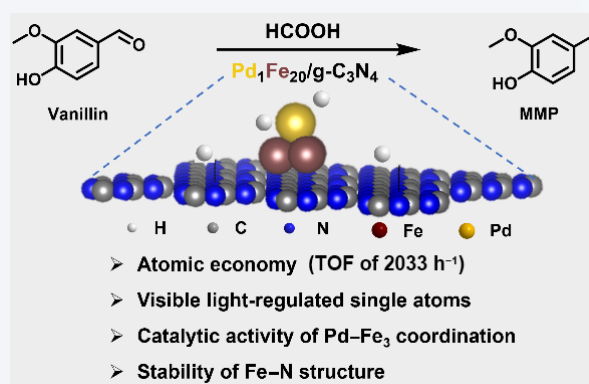
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ABSTRACT: The development of efficient catalytic hydrodeoxygenation (HDO) processes for vanillin offers a promising but technically demanding approach to generating 2-methoxy-4-methylphenol (MMP). The as-prepared Pd₁Fe₂₀/graphitic carbon nitride (g-C₃N₄) single atom catalyst was synthesized by photo-deposition strategy and enabled the HDO to obtain conversion 99% and MMP selectivity of 99%, achieving a turnover frequency (TOF) of 2033 h⁻¹. Characterization via X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) confirmed the existence of Fe clusters, Pd single atoms, and a well-defined Pd–Fe₃ coordination. Density functional theory (DFT) simulations further provided insights into the electronic configuration of the Pd sites, demonstrating that the Pd–Fe₃ interaction strengthens substrate adsorption and reduces the energy barrier for the rate-limiting step. This study not only addresses the overreliance on precious metals but also establishes a guided approach for designing single atom catalysts for the conversion of biomass-derived feedstocks.



KEYWORDS: hydrodeoxygenation, heterogeneous, photocatalysis, single atoms, selectivity, vanillin

1 Introduction

To deal with climate change and energy demands in the future, exploring the catalytic conversion (Conv.) of biomass-derived lignin to produce value-added chemicals is considered an important solution to reduce reliance on fossil resources [1–4]. As a platform chemical derived from lignin, 4-hydroxy-3-methoxybenzaldehyde (vanillin) is often used to produce 2-methoxy-4-methylphenol (MMP), which is an intermediate for many high-value-added drugs and fragrances, through catalytic hydrodeoxygenation (HDO) [5–7]. Therefore, the development of efficient catalytic system for the HDO process of vanillin to MMP is an inevitable requirement for production and green chemistry.

In the past decade, the catalytic HDO of vanillin has mainly focused on heterogeneous catalysis, and a series of catalysts (such as Pd [8–11], Pt [12], Ni [13], and Co [14, 15] nanoparticles (NPs)) have been developed to conduct transformation of vanillin under high-pressure H₂. This process exhibits dangers and low efficiency

associated with hydrogen storage, and leads to the formation of by-products. Recently, formic acid has been regarded as a relatively green hydrogen source in biomass transformation and used for the catalytic transfer hydrogenation of vanillin under mild conditions [14, 16, 17]. Wu et al. [17] reported 1.5 wt.% Pd–Au bimetallic nanoparticles catalyst for MMP, affording yield of 98% and turnover frequency (TOF) of 378 h⁻¹. Meanwhile, the photocatalytic conversion of vanillin provided green pathway for sustainable chemistry. Varma et al. [18] designed 4.6 wt.% Ag–Pd nanoparticle catalysts for HDO of vanillin under visible light, achieving yield of 99% and TOF of 69 h⁻¹. Obviously, researchers have made efforts to improve the Pd-based catalysts in HDO process (Table S1 in the Electronic Supplementary Material (ESM)). However, the poor dispersion and the excessive use of precious metal nanoparticles lead to severe agglomeration, resulting in low cost-effectiveness and restricting their practical application [19–22]. Therefore, the development of catalysts with optimized atomic utilization is essential for the HDO of vanillin.

In recent years, single atom catalysts have attracted much attention due to their characteristics, such as highly exposed atomic surfaces and high atomic utilization [23–25]. Li et al. [6] reported Pd₁/WO_{2.72} catalysts for HDO process of 0.08 mmol vanillin under 1 MPa H₂, affording MMP yield of 99%. Ouyang et al. [23] designed Pd₁/covalent organic frameworks (COF) catalysts for

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hydrogenative hydrogenolysis of aromatic aldehydes, achieving MMP yield of 99% and TOF lower than 100 h^{-1} . Later, Pang et al. [24] constructed Pd single atoms supported on lignin-functionalized phenolic resin for transition of vanillin with TOF lower than 100 h^{-1} . It revealed the highly efficient and specific role of Pd single atoms for HDO process. The construction of these single atom catalysts pays more attention to the pursuit of functionalized supports, neglecting the synergistic effect of Pd single atoms with co-catalysts for higher catalytic activity. Recent studies highlight that constructing single atom catalysts in synergy with nanoparticles or clusters is a practical and effective solution, which influences the electronic structure and enhances the catalytic ability [26–29]. Shi et al. [26] reported that combination of nanoparticles with single metal sites synergistically boosts co-catalyzed formic acid dehydrogenation. Excitedly, the application of such systems in photocatalytic hydrogen transfer reactions, particularly HDO of vanillin, has remained largely unexplored.

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), with its extended π -conjugated system and excellent metal coordination ability, has become a common carrier for photocatalysts [30, 31]. Single atoms are typically dispersed on $\text{g-C}_3\text{N}_4$ to promote its extremely exceptional charge separation capacity [32]. The support's absorption capacity of visible light is often enhanced with Fe nanoparticles or clusters owing to its suitable energy band position [33, 34]. Therefore, we anticipate a strategy that enhances the light absorption capacity of $\text{g-C}_3\text{N}_4$ by introducing Fe atoms and then anchoring Pd single atoms in the system through photo-deposition, which will significantly improve the coordination environment of Pd atoms and promote the redistribution of charges. In this study, we report a photo-deposition method for the controlled construction of Pd single atoms through broad support's light absorption in the long-wavelength region. The resulting $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ single atom catalyst coupled with Fe clusters was successfully synthesized under irradiation at 520 nm, where Pd was predominantly present as Pd^{2+} with loading of 0.24 wt.%. The light-driven HDO process on $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ achieved conversion of 99% and MMP selectivity of 99%, and reached TOF of 2033 h^{-1} , surpassing the literature reports. The presence of Pd single atoms and the Pd–Fe₃ coordination structure were confirmed by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses, both of which contributed to the observed catalytic performance. Density functional theory (DFT) calculations further elucidated the electronic properties of the Pd centers and revealed that the Pd–Fe₃ coordination enhances reactant adsorption and lowers the activation energy barrier. This approach addresses the challenge of excessive noble metal usage and offers a rational design strategy for single atom catalysts in biomass-derived lignin transformations.

2 Experimental section

2.1 Materials and methods

2.1.1 Chemicals

Melamine, ferric chloride (FeCl_3), palladium chloride (PdCl_2), formic acid, and vanillin were provided by Macklin Biochemical Technology. Ammonium hydrogen carbonate (NH_4HCO_3) was provided by Adamas. All reagents used in this study were analytical grade and utilized without further purification.

2.1.2 Evaluation of catalytic performance

The hydrogenation deoxygenation process of vanillin was conducted in a set of commercial photo-reactors (Titan self-developed). Typically, vanillin (1 mmol), formic acid (2.5 mmol), and the prepared $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (15 mg) were introduced into a Schlenk pipe, including deionized water (6 mL) and ethyl acetate (EA, 3 mL). When adsorption reached equilibrium without light, the system was subjected to irradiation for 5 h in N_2 environment. The products were extracted with ethyl acetate and assessed by high-performance liquid chromatography (HPLC) after completion.

2.2 Preparation of catalysts

2.2.1 Synthesis of 2.5 wt.% $\text{Fe}_{\text{NP}}/\text{g-C}_3\text{N}_4$

FeCl_3 (37 mg) was thoroughly mixed with melamine (1 g) by the impregnation method. Mixture along with NH_4HCO_3 (2 g) was placed in crucibles, subsequently heated to 550°C at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$, and maintained at that temperature for 4 h. It was then heated to 300°C for 2 h with a rate of $3^\circ\text{C}\cdot\text{min}^{-1}$ under 5% H_2/N_2 after cooling. The resulting grey solids were washed, centrifuged, and subsequently dried.

2.2.2 Synthesis of 0.24 wt.% $\text{Pd}_{1+\text{NP}}/\text{g-C}_3\text{N}_4$

PdCl_2 (1 mg) was thoroughly mixed with $\text{g-C}_3\text{N}_4$ (0.25 g) by the impregnation method. Mixture and isopropyl alcohol (15 mL) were added into a Schlenk pipe and exposed to visible light (413 nm) for 6 h under N_2 atmosphere. Upon completion, the obtained grey products were washed, centrifuged, and then dried at 60°C for 12 h. Generally, the final obtained catalysts were named $\text{Pd}_{1+\text{NP}}/\text{g-C}_3\text{N}_4$.

2.2.3 Synthesis of $\text{Pd}_1\text{Fe}_{\text{NP}}/\text{g-C}_3\text{N}_4$

PdCl_2 (1 mg) was thoroughly mixed with $\text{Fe}_{\text{NP}}/\text{g-C}_3\text{N}_4$ (0.25 g) by the impregnation method. Mixture and isopropyl alcohol (15 mL) were added into a reactor and subjected to irradiation (520 nm) for 6 h under N_2 environment. The resulting grey solids were washed and dried. Generally, the final obtained catalysts were named $\text{Pd}_1\text{Fe}_x/\text{g-C}_3\text{N}_4$, where x represented the atomic ratio of Fe to Pd. In addition, we prepared the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ under irradiation of light sources with different wavelengths (369, 396, 413, 460, 520, 590, 623 nm) with similar methods, respectively named $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (369 nm), $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (396 nm), $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$, $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (460 nm), $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (520 nm), $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (590 nm), and $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (623 nm).

As shown in Fig. 1, the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ catalyst was prepared by calcination-annealing and photo-deposition methods. The synthesis and characterization details of the catalyst can be found in the ESM.

3 Results and discussion

3.1 Structural characterization

The X-ray diffraction (XRD) patterns of the composite materials closely matched the simulated results, suggesting that these catalysts exhibited a high level of crystallinity (Fig. 2(a)). All catalysts exhibited diffraction peaks located at 13.0° and 27.5° , assignable to the (100) and (002) crystal facets of $\text{g-C}_3\text{N}_4$, respectively. The (100) peak at 13.0° was associated with the presence of triazine rings within the layers, whereas the more prominent (002) peak at 27.5° was linked to the π – π stacking interactions between the conjugated

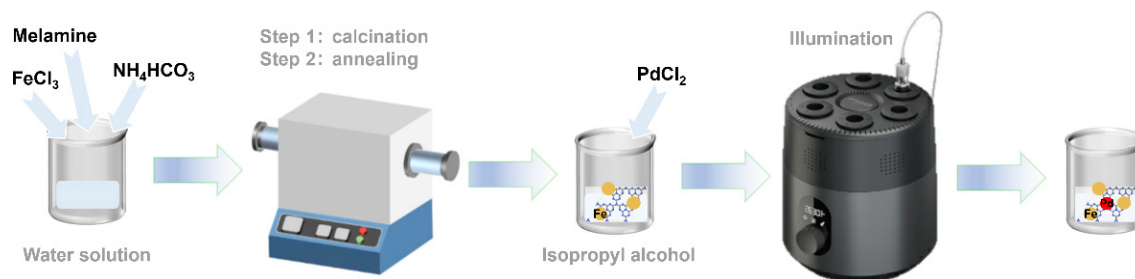


Figure 1 The preparation process of the catalyst.

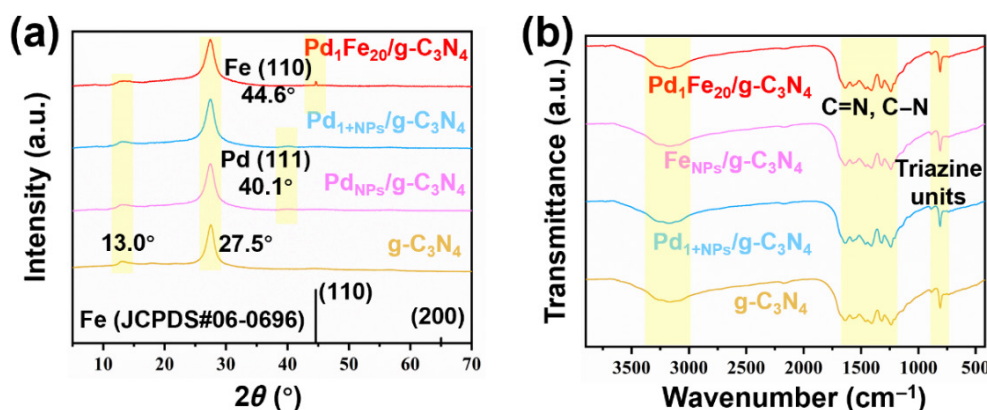


Figure 2 (a) XRD patterns and (b) FT-IR spectra of samples.

aromatic structures, similar to the stacking observed in graphene [35]. The characteristic peak of Pd (111) was observed in both $\text{Pd}_{\text{NP5}}/\text{g-C}_3\text{N}_4$ and $\text{Pd}_{1+\text{NP5}}/\text{g-C}_3\text{N}_4$, as the single atoms are highly dispersed and lack long-distance ordered crystal structures [36]. In addition, the characteristic peak of Fe (110) was observed in $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ at 44.6° , indicating that Fe was successfully introduced without changing the crystal structure of $\text{g-C}_3\text{N}_4$ [37]. In comparison with $\text{Pd}_{1+\text{NP5}}/\text{g-C}_3\text{N}_4$, the introduction of Fe clusters in $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ promoted the formation of Pd single atoms. The chemical functional groups and compositional characteristics of the composites were further investigated through Fourier transform infrared (FT-IR) spectroscopy (Fig. 2(b)). The absorption band in the range of $700\text{--}1000\text{ cm}^{-1}$ corresponds to the out-of-plane deformation vibration of the triazine ring, whereas the peak around 1500 cm^{-1} is associated with the stretching mode of C–N bonds in heterocyclic structures [38]. Although characteristic peaks of Fe–N coordination were not observed, neither were the Fe–O stretching vibration peaks (near 540 and 450 cm^{-1}) and Pd–O vibration peaks detected, due to the low content of the doped metals.

Transmission electron microscopy (TEM) of $\text{Fe}_{\text{NP5}}/\text{g-C}_3\text{N}_4$ and $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ showed that Fe nanoparticles were well dispersed on the surface of the support, and the introduction of Pd did not lead to metal agglomeration compared with $\text{Fe}_{\text{NP5}}/\text{g-C}_3\text{N}_4$ (Figs. 3(a)–3(c)). TEM image shows that the lattice spacings of 0.20 nm corresponded to the (110) facets of Fe clusters, which possessed a particle size of approximately 2.5 nm (Fig. 3(d)) [37]. High-magnification high-angle annular dark-field scanning TEM (HAADF-STEM) image distinctly illustrates the ordered dispersion of Pd and Fe atoms within the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ spheres, where Pd atoms exhibited a brighter contrast compared to Fe atoms (Fig. 3(e)). The intensity profile along the blue and red lines further verified the alternating arrangement of Pd and Fe atoms, as the signal intensity was roughly proportional to the square of their

respective atomic numbers (Fig. 3(f)) [28]. Energy dispersive X-ray spectroscopy (EDS) mapping images corresponding to TEM image present a uniform distribution of Pd, Fe, C, and N elements in $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (Fig. 3(g)). Compared to $\text{Pd}_{1+\text{NP5}}/\text{g-C}_3\text{N}_4$, the introduction of Fe clusters enabled the Pd element to be highly dispersed without agglomeration (Fig. S1 in the ESM), and the content of the elements was almost the same as the theoretical amount in the preparation process (Fig. S2 in the ESM). $\text{Fe}_{\text{NP5}}/\text{g-C}_3\text{N}_4$, $\text{Pd}_{1+\text{NP5}}/\text{g-C}_3\text{N}_4$, and $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ retained the basic physical properties of $\text{g-C}_3\text{N}_4$, which allowed them a high specific surface area, providing more active metal sites (Table S10 in the ESM). To compare the Pd metal dispersion of different catalysts, CO adsorption was performed (Table S12 in the ESM). Pd metal dispersion of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ was 70.21% , which is much higher than that of $\text{Pd}_{1+\text{NP5}}/\text{g-C}_3\text{N}_4$, demonstrating the superiority of Fe and visible-light deposition for the formation of Pd single atoms.

X-ray photoelectron spectroscopy (XPS) spectra were conducted to detect the binding energy and valence states of C 1s, N 1s, Fe 2p, and Pd 3d (Fig. 4(a)). Compared with pure $\text{g-C}_3\text{N}_4$, the binding energy of C 1s and N 1s in the other samples all exhibited a shift toward lower values, meaning stronger charge transfer capacity (Figs. 4(b) and 4(c)). Additionally, the Fe 2p spectrum of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ can be deconvoluted into two doublets corresponding to Fe^{2+} and Fe^{3+} . It was observed that 723.5 and 710.6 eV correspond to the orbitals of $\text{Fe}^{2+} 2p_{1/2}$ and $2p_{3/2}$, and 726.6 and 713.5 eV correspond to the orbitals of $\text{Fe}^{3+} 2p_{1/2}$ and $2p_{3/2}$, respectively (Fig. 4(d)) [39]. $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ exhibited a reduced binding energy of Fe 2p, indicating that Fe atoms received more electron transfer from Pd, compared to $\text{Pd}_{1+\text{NP5}}/\text{g-C}_3\text{N}_4$. The presence of more Fe^{3+} indicates that more Fe–O shells are formed in the Fe clusters with doping of Pd atoms, enhancing the adsorption capacity for the substrate. Moreover, weak peaks of 342.3 and 337.0 eV correspond to the $\text{Pd}^{2+} 3d_{3/2}$ and $3d_{5/2}$ orbitals, and strong peaks of 340.1 and 334.8 eV correspond to the $\text{Pd}^0 3d_{3/2}$ and $3d_{5/2}$ orbitals, which implied the

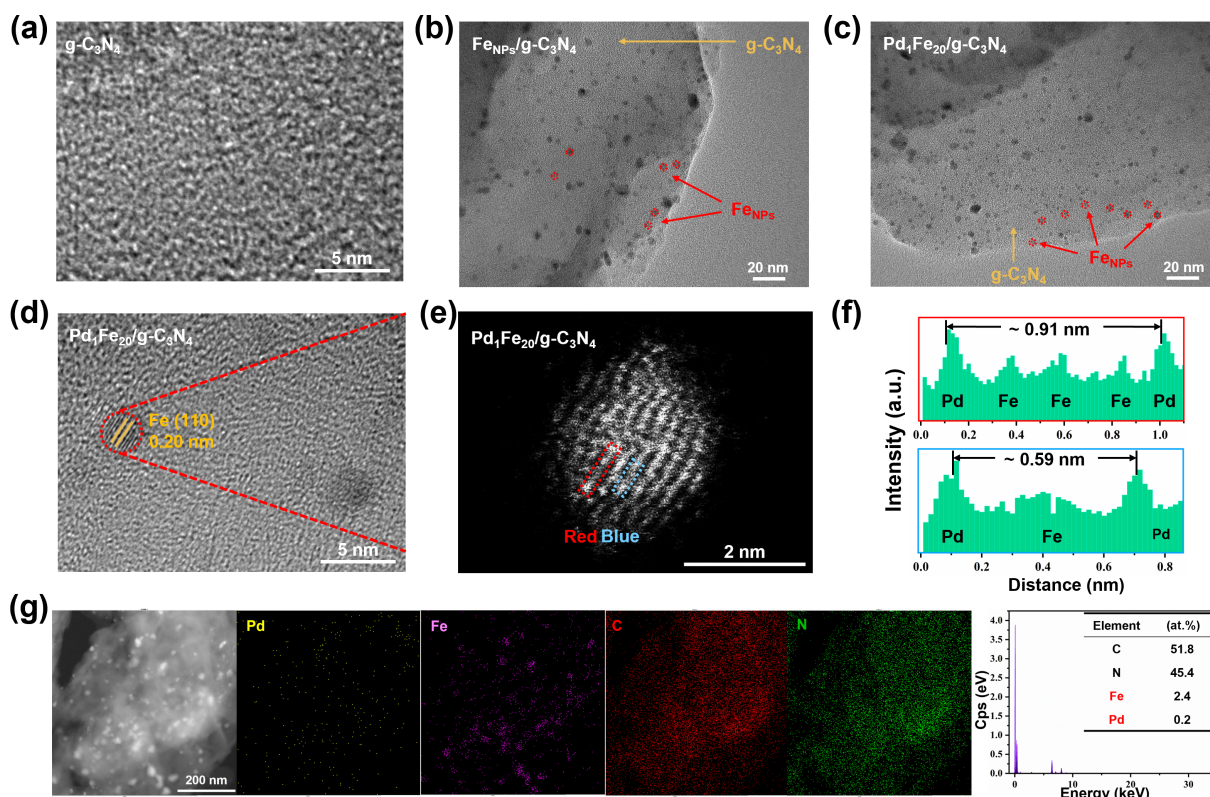


Figure 3 TEM images of (a) $g-C_3N_4$, (b) $Fe_{NP}/g-C_3N_4$, ((c) and (d)) $Pd_1Fe_{20}/g-C_3N_4$. ((e) and (f)) HAADF-STEM image of $Pd_1Fe_{20}/g-C_3N_4$ and corresponding intensity profiles. (g) EDS mapping images of $Pd_1Fe_{20}/g-C_3N_4$.

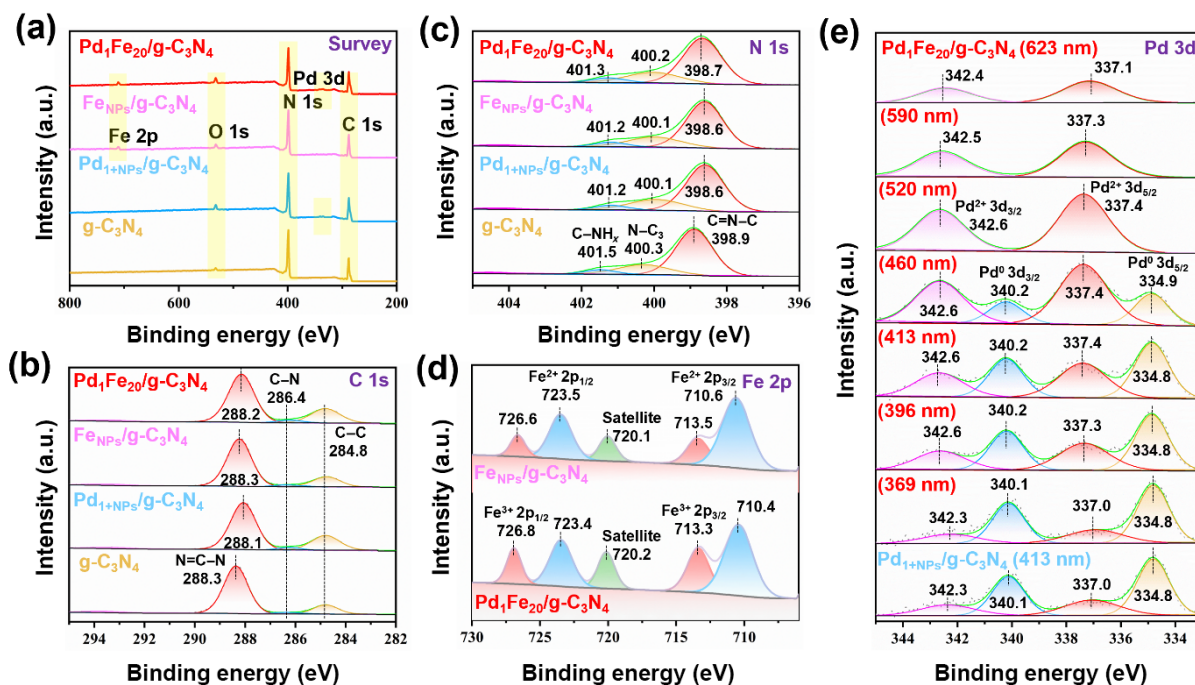


Figure 4 XPS spectra of $Pd_1Fe_{20}/g-C_3N_4$: (a) survey, (b) C 1s, (c) N 1s, (d) Fe 2p, and (e) Pd 3d XPS spectra of $Pd_{1+NP}/g-C_3N_4$ (413 nm) and $Pd_1Fe_{20}/g-C_3N_4$ (369, 396, 413, 460, 520, 590, and 623 nm).

presence of a large number of Pd nanoparticles in the $Pd_{1+NP}/g-C_3N_4$ (413 nm) (Fig. 4(e)) [40, 41]. The introduction of Fe atoms broadened the light absorption range of samples, so we prepared a series of $Pd_1Fe_{20}/g-C_3N_4$ catalysts under different wavelengths (369, 396, 413, 460, 520, 590, and 623 nm). It was observed that 342.6 and

337.4 eV correspond to the orbitals of $Pd^{2+} 3d_{3/2}$ and $3d_{5/2}$, respectively, indicating the existence of Pd single atoms or Pd-O in the $Pd_1Fe_{20}/g-C_3N_4$ (520 nm), which requires more evidence to identify. As the wavelength of the light increased during the photo-deposition process, the proportion of Pd atoms also increased

(Table S3 in the ESM). This was attributed to the low energy of long-wave light, which significantly suppressed the process of atomic agglomeration [42]. Furthermore, Pd atoms were also prepared under 590 and 623 nm, but the loading amounts were only 0.07% and 0.04%, due to the insufficient energy of long-wave (Table S2 in the ESM). Compared with $\text{Pd}_{1+\text{NP}}/\text{g-C}_3\text{N}_4$, the binding energy of Pd 3d in the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (520 nm) demonstrated a shift toward higher values, which implied that electrons were transferred from Pd to Fe atoms, resulting in an increase in valence state (Fig. 4(e)) [19, 43]. Obviously, it provided proof for the existence of Pd-Fe coordination.

To study the valence state and coordination structure, XANES and EXAFS spectroscopy analyses were conducted. On the one hand, the position of the Fe K-edge absorption in the XANES reflected the average oxidation state of Fe species, and the energy absorption edge of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ was located between FeO and Fe_3O_4 , suggesting the oxidation state of Fe is between +2 and +3 (Fig. 5(a)) [44, 45]. EXAFS of Fe clusters showed characteristic peaks at 1.8 and 2.7 Å, corresponding to Fe-O and Fe-Fe coordination on the outer shell. Peaks at 1.6 and 2.2 Å were attributed to Fe-N and Fe-Fe coordination on the inner shell, respectively (Fig. 5(b)). Quantitative fitting of the EXAFS spectra revealed that the average length of the Fe-N bond was 1.94 Å with coordination number of 1.34, and average length of the Fe-Fe bond was 2.48 Å with coordination number of 2.31 on the inner shell (Fig. 5(c) and Table S4 in the ESM). Through careful consideration, we believed that the Fe atoms in the inner layer are more likely to form coordination with the Pd atoms. On the other hand, XANES showed that the energy absorption edge of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ was close to that of PdO, indicating that the valence state of Pd was very close to Pd^{2+} , which is consistent with the results of XPS (Fig. 5(d)) [24]. In addition, EXAFS of Pd foil displayed characteristic peak at 2.5 Å, corresponding to Pd-Pd scattering coordination (Fig. 5(e)). Peaks at 1.6 and 3.1 Å were attributed to Pd-O and Pd-Pd of the first coordination shell, respectively. The absence of Pd-Pd bonding confirmed that Pd existed in the form of single atoms in $\text{Pd}_1\text{Fe}_{20}/$

$\text{g-C}_3\text{N}_4$, while the characteristic peak at 2.4 Å was related to Pd-Fe coordination, in agreement with the XPS results [28]. Quantitative fitting of the EXAFS spectra of Pd revealed that the average length of the Pd-Fe bond was 2.66 ± 0.02 Å, and the coordination number of Pd-Fe was 3.3 (Fig. 5(f) and Table S5 in the ESM). The EXAFS spectra displayed Pd-N coordination with number of 0.3, which was derived from Pd atoms and N of $\text{g-C}_3\text{N}_4$. Additionally, electron paramagnetic resonance (EPR) was performed to further verify the existence of nitrogen vacancies (Nv). Characteristic signal ($g = 2.003$) was observed in the spectra, indicating that a small amount of nitrogen vacancy is introduced (Fig. S8 in the ESM) [46]. The presence of nitrogen vacancies can enhance the adsorption capacity for reactants. Based on the above discussion, we propose a reasonable structure of $\text{Pd-Fe}_3\text{-N}_3$ for the reaction sites within the inner shell (Fig. 5(f)). These results indicated that the Fe-N coordination in the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ catalyst ensured stability, while the Pd- Fe_3 coordination formed by Pd single atoms further enhanced the reaction activity.

3.2 Optical and electrochemical properties

Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was performed to evaluate the optical absorption behavior of samples. The typical absorption edge near 390 nm was attributed to an intrinsic electron leap ($\pi \rightarrow \pi^*$) of $\text{g-C}_3\text{N}_4$, but its absorption capacity for visible light dropped sharply, to the extent that there was almost no absorption around 450 nm (Fig. 6(a)) [47]. Excitingly, with the loading of Fe clusters, the absorption intensity for long wavelengths significantly increased, due to the coordination of Fe 2d orbitals with the lone pair electrons provided by nitrogen for a stable Fe-N bond. Based on the above capabilities, we were able to prepare a series of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ catalysts under different wavelengths, all of which possessed excellent visible light absorption, compared to $\text{Pd}_{1+\text{NP}}/\text{g-C}_3\text{N}_4$. Additionally, the optical band gaps (E_g) were determined using the Kubelka-Munk formula (Eq. (S1) in the ESM) for $\text{g-C}_3\text{N}_4$, $\text{Pd}_{1+\text{NP}}/\text{g-C}_3\text{N}_4$, $\text{Fe}_{\text{NP}}/\text{g-C}_3\text{N}_4$, and $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ samples were 2.67, 2.64, 2.58, and 2.50 eV,

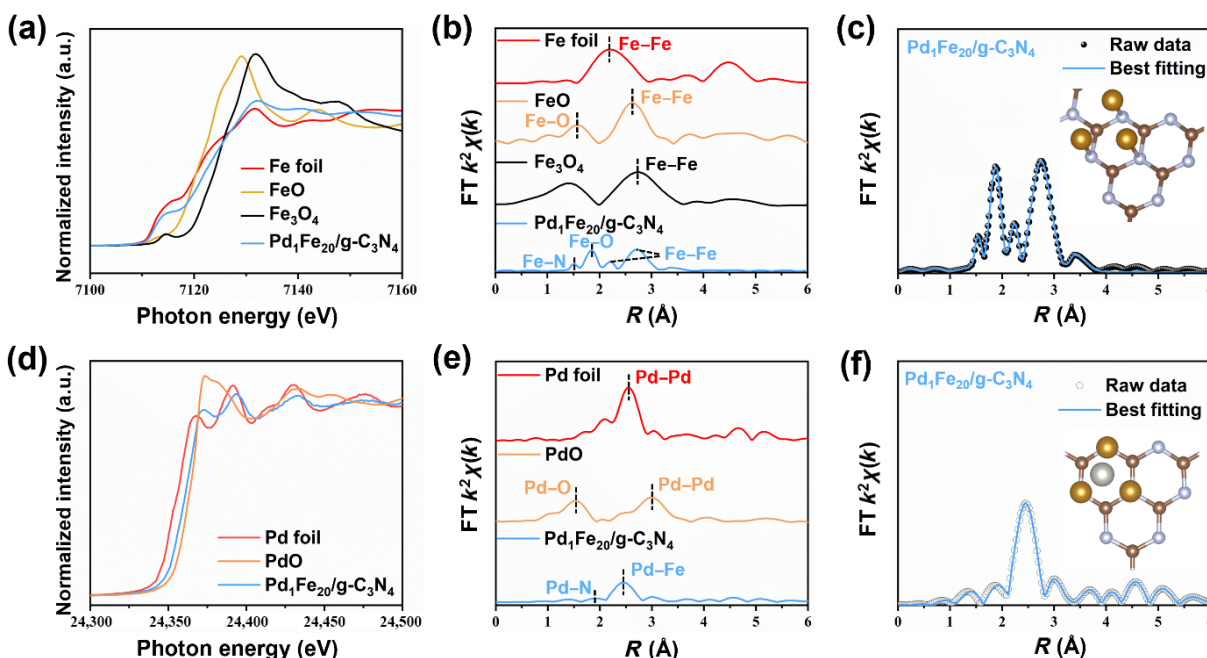


Figure 5 (a) Fe K-edge XANES spectra and (b) FT k^2 -weighted EXAFS spectra of Fe foil, FeO, and $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$. (c) Fe and (f) Pd EXAFS fitting curves of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ in R space. (d) Pd K-edge XANES spectra and (e) FT k^2 -weighted EXAFS spectra of Pd foil, PdO, and $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$.

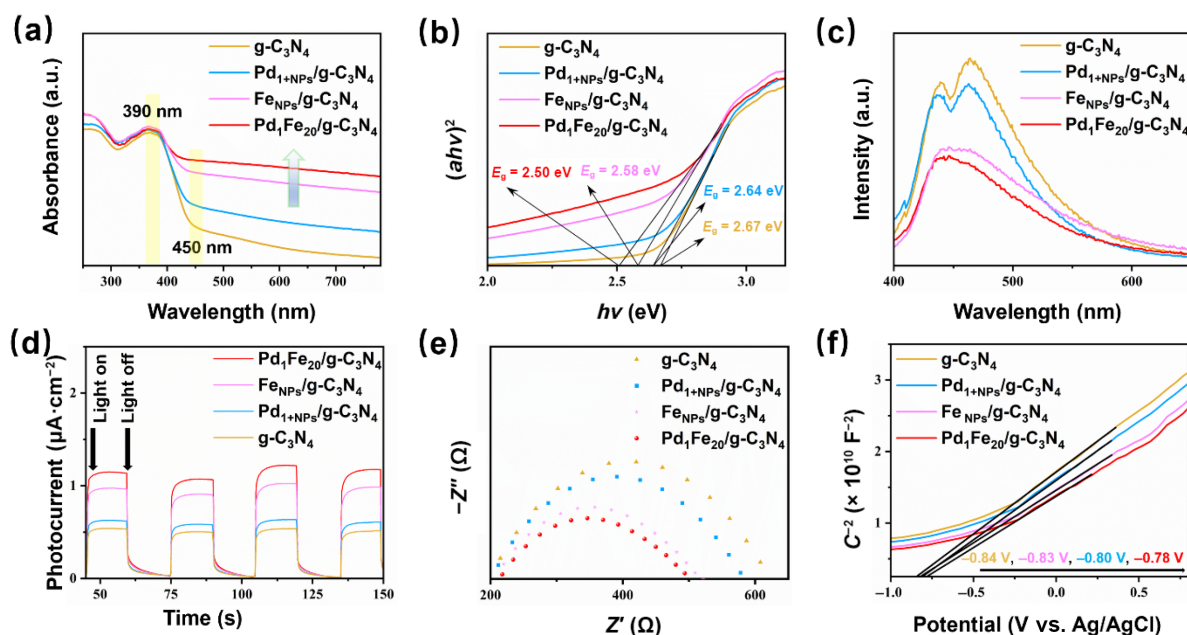


Figure 6 (a) UV-vis DRS spectra, (b) Tauc plots, (c) PL spectra, (d) photocurrent responses, (e) EIS curves, and (f) Mott-Schottky plots of g-C₃N₄, Pd_{1+NP5}/g-C₃N₄, Fe_{NP5}/g-C₃N₄, and Pd₁Fe₂₀/g-C₃N₄.

respectively, providing more feasibility evidence for generating Pd single atoms through the regulation of light wavelength (Fig. 6(b)). A distinct and intense emission peak was detected around 450 nm in the photoluminescence (PL) spectra, attributed to the electronic transition occurring within the conjugated aromatic structure of g-C₃N₄ [48]. Obviously, the emission peak of Fe_{NP5}/g-C₃N₄ was significantly reduced, which means the introduction of Fe clusters effectively promotes the separation of photogenerated charges (Fig. 6(c)). Meanwhile, Pd₁Fe₂₀/g-C₃N₄ catalyst exhibited the strongest photocatalytic performance. Photocurrent-time curves provided the same findings as PL: Pd₁Fe₂₀/g-C₃N₄ catalyst possessed strongest charge separation capability, due to Pd-Fe coordination (Fig. 6(d)) [3]. Electrochemical impedance spectroscopy (EIS) was conducted to further verify these findings. Pd₁Fe₂₀/g-C₃N₄ displayed the smallest arc radius, suggesting the lowest photo-induced electrical impedance and the most efficient separation of photogenerated charge carriers (Fig. 6(e)). The energy band positions of g-C₃N₄, Pd_{1+NP5}/g-C₃N₄, Fe_{NP5}/g-C₃N₄, and Pd₁Fe₂₀/g-C₃N₄ samples were characterized through Mott-Schottky plots, which showed n-type semiconductor behaviors as positive slopes were observed (Fig. 6(f)). Typically, flat-band potentials (E_f) are situated approximately 0.1 V more positive than the conduction band potentials (E_{CB}) of an n-type semiconductor. E_f of samples were -0.84, -0.80, -0.83, and -0.78 V, and the corresponding E_{CB} were -0.94, -0.90, -0.93, and -0.88 V with respect to the Ag/AgCl electrode, respectively. Consequently, E_{CB} were -0.74, -0.70, -0.73, and -0.68 V relative to the normal hydrogen electrode (NHE), according to Eq. (S2) in the ESM. Valence band positions (E_{VB}) of g-C₃N₄, Pd_{1+NP5}/g-C₃N₄, Fe_{NP5}/g-C₃N₄, and Pd₁Fe₂₀/g-C₃N₄ were 1.93, 1.94, 1.85, and 1.82 V (vs. NHE), respectively (Eq. (S3) in the ESM).

3.3 Investigation of catalytic performance

On the one hand, the catalytic performance of Pd_{1+NP5}/g-C₃N₄ in the HDO of vanillin was analyzed in aqueous solution with formic acid as hydrogen source, compared to Pd_{NP5}/g-C₃N₄. We recognized that the excellent catalytic activity of Pd single atoms in the

hydrogenation of vanillin to 4-hydroxy-3-methoxyphenyl methanol (HMP) was compared with Pd nanoparticles (Table S6 in the ESM, Entries 3–5). Control experiments in different solvents showed that H₂O/EA in a volume ratio of 2:1 can efficiently produce HMP, with the highest yield of 46% (Table 1, Entry 1; and Table S6 in the ESM, Entries 6 and 7). Studies on the different supports of Pd single atoms revealed that g-C₃N₄ is indispensable (Table S6 in the ESM, Entries 8 and 9). Unfortunately, further hydrogenolysis of HMP to MMP was difficult on the Pd_{1+NP5}/g-C₃N₄ in the absence of other co-catalysts (Fig. 7(a)).

On the other hand, Pd₁Fe₂₀/g-C₃N₄ afforded a HDO pathway involving hydrogenation to HMP followed by -CH₂OH hydrogenolysis to MMP. After 5 h, vanillin was completely converted to MMP with a yield of 99% and the highest TOF of 2033 h⁻¹ over Pd₁Fe₂₀/g-C₃N₄ (Table 1, Entry 6 and Fig. 7(b)). Initially, we found that the introduction of Fe clusters effectively enhanced the absorption capacity of g-C₃N₄ for visible light. We adjusted the most crucial parameter of wavelength (369, 396, 413, 460, 520, 590, 623 nm) during photo-deposition to regulate the growth of Pd single atoms and increase its proportion with different catalytic activation (Fig. 7(c)). When the wavelength increased from 369 to 520 nm, the catalytic activity significantly improved with yield of 18% to 99%, as the proportion of Pd single atoms increased under long-wavelength irradiation (Table 1, Entries 2–6). When the wavelength increased from 520 to 623 nm, the catalytic activity dropped sharply with yield of 99% to 10%, as the Pd active sites decreased due to insufficient energy (Table 1, Entries 6 and 8). With the deposition wavelength of 520 nm, Pd₁Fe₂₀/g-C₃N₄ possessed the optimal single-atom ratio and Pd active sites, which had been verified by XPS and inductively coupled plasma-mass spectrometry (ICP-MS) (Tables S2 and S3 in the ESM). Notably, the yield of MMP increased with increasing Pd/Fe ratio and achieved 99% at a ratio of 1/20, while the TOF decreased to 949 h⁻¹ at a ratio of 1/5 (Table 1, Entries 9–12). At the Pd/Fe ratio of 1/20, the TOF of MMP increased with increasing Pd content and achieved 2033 h⁻¹ at 0.24 wt.%, with TOF decreasing to 1153 h⁻¹ at 0.94 wt.% (Table 1, Entries 13–15).

Table 1 Photocatalyst evaluation for HDO of vanillin^a

		Vanillin		MMP		HMP		
Entry	Catalyst	Loading (wt.%)		Deposition wavelength (nm)	Conv. (%) ^b	Yield (%) ^b		TOF ^c (h ⁻¹)
		Pd	Fe			MMP	HMP	
1 ^d	Pd ₁ +NiP ₃ /g-C ₃ N ₄	0.24	0	413	46	—	46	492
2	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.24	2.5	369	46	18	28	523
3	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.24	2.5	396	49	29	20	566
4	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.24	2.5	413	61	53	8	874
5	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.24	2.5	460	76	71	5	1254
6	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.24	2.5	520	99	99	—	2033
7	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.24	2.5	590	32	32	—	376
8	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.24	2.5	623	11	10	1	130
9 ^e	Pd ₁ Fe ₅ /g-C ₃ N ₄	0.93	2.5	520	99	99	—	1090
10 ^f	Pd ₁ Fe ₁₀ /g-C ₃ N ₄	0.47	2.5	520	99	99	—	1637
11	Pd ₁ Fe ₃₀ /g-C ₃ N ₄	0.16	2.5	520	47	40	7	988
12	Pd ₁ Fe ₄₀ /g-C ₃ N ₄	0.12	2.5	520	34	31	3	949
13	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.12	1.3	520	31	30	1	918
14 ^g	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.48	5	520	99	99	—	1600
15 ^h	Pd ₁ Fe ₂₀ /g-C ₃ N ₄	0.94	10	520	99	98	1	1153

^aReaction conditions: vanillin (1 mmol), formic acid (2.5 mmol), photocatalyst (15 mg), solvent (H₂O, 6 mL; EA, 3 mL), 15 W LED with 413 nm, N₂, room temperature, and 5 h. ^bConversion and yield were determined by HPLC. ^cCalculated at 10% conversion of the substrate based on the active sites present in the catalyst. ^dFormic acid (1.5 mmol) and 8 h. ^e2 h. ^f3 h. ^g2 h.

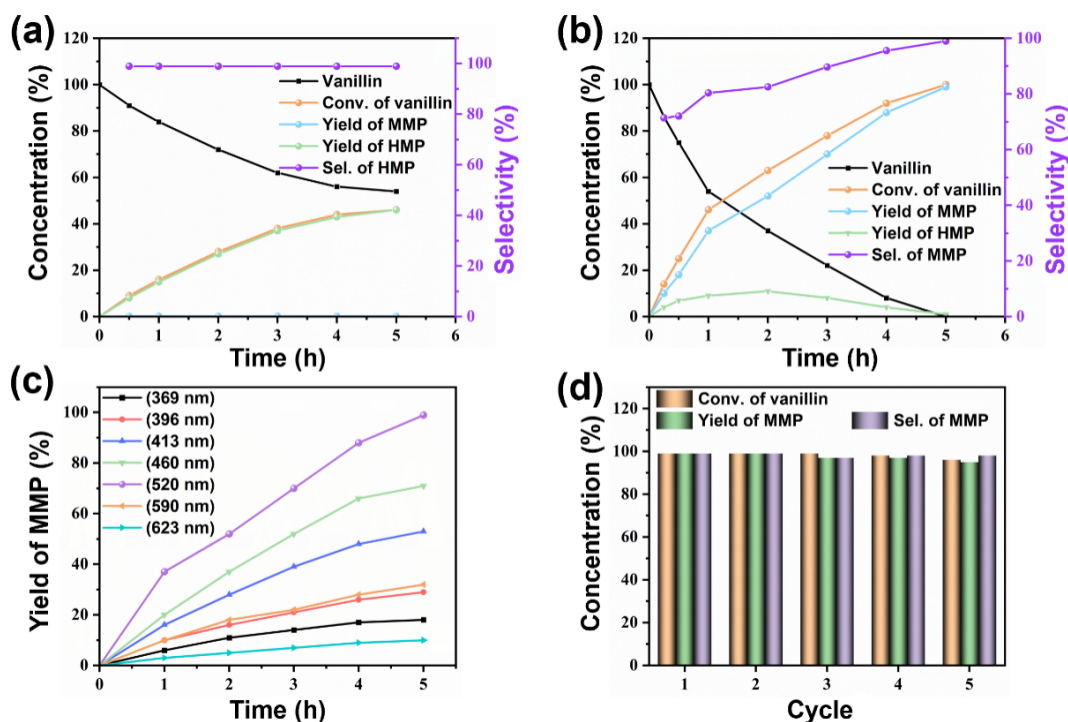


Figure 7 Concentration of vanillin, MMP, and HMP, conversion of vanillin, and selectivity of products on the (a) Pd₁NiP₃/g-C₃N₄ (Nv) and (b) Pd₁Fe₂₀/g-C₃N₄. (c) Yield of MMP on the Pd₁Fe₂₀/g-C₃N₄ deposited at different wavelengths. (d) Cycling stability of Pd₁Fe₂₀/g-C₃N₄.

Subsequently, some reaction parameters (i.e., solvent, formic acid content, wavelength, and power) were optimized. H₂O/EA in a volume ratio of 2:1 can also efficiently obtain MMP with yield of 85%, compared with other solvents, including H₂O, ethanol

(EtOH), and EA (Table S6 in the ESM, Entries 11–14). As the formic acid content decreased from 4 to 2 mmol, the yield increased and reached 99% at 2.5 mmol, but then dropped to 71% at 2 mmol (Table S6 in the ESM, Entries 15–17). Generally, the

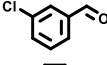
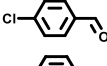
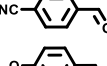
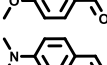
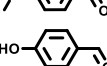
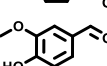
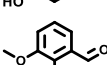
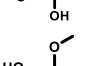
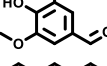
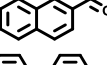
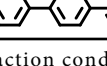
efficiency of formic acid reached 70% to 80% in our mild catalytic system, which exceeded the catalytic system reported. Compared with the yields at long wavelengths (460 and 520 nm), which were 69% and 39%, both 369 and 413 nm achieved yield of 99%, among which 413 nm was considered sustainable (Table S6 in the ESM, Entries 18–20). As the power of the light-emitting diode (LED) decreased from 15 to 6 W, the yield of MMP dropped from 99% to 23% (Table S6 in the ESM, Entries 21–23). In addition, Co, Ni, and Cu co-catalysts were considered to prepare $\text{Pd}_1\text{Co}_{20}/\text{g-C}_3\text{N}_4$, $\text{Pd}_1\text{Ni}_{20}/\text{g-C}_3\text{N}_4$, and $\text{Pd}_1\text{Cu}_{20}/\text{g-C}_3\text{N}_4$; TiO_2 and SiC were used to prepare $\text{Pd}_1\text{Fe}_{20}/\text{TiO}_2$ and $\text{Pd}_1\text{Fe}_{20}/\text{SiC}$, respectively (Table S6 in the ESM, Entries 24–28). All of them possessed catalytic activity for the hydrogenation of vanillin to HMP. Furthermore, the mixture of $\text{Pd}_{1+\text{NP}_8}/\text{g-C}_3\text{N}_4$ and $\text{Fe}_{\text{NP}_8}/\text{g-C}_3\text{N}_4$ did not catalyze the generation of MMP either (Table S6 in the ESM, Entry 29).

To evaluate the scalability of the reaction, the amount of vanillin was increased to 10 mmol and the HDO process was carried out for 16 h on 150 mg of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$, achieving yield of 71% and TOF of 262 h^{-1} (Table S1 in the ESM). $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ reached TOF of $13,119 \text{ h}^{-1}$ when vanillin was 0.1 mmol. Additional recycling experiments were conducted to evaluate stability of catalysts. $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ displayed satisfactory stability before and after five cycles in both vanillin conversion and MMP selectivity (Fig. 7(d)). ICP-MS of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ after cycle experiments showed the contents of Pd and Fe were almost the same as before the reaction (Table S7 in the ESM). It was observed that the absence of Pd nanoparticles and metal agglomeration in TEM image indicated the structural stability of the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ (Fig. S9 in the ESM). Moreover, $\text{Pd}_{1+\text{NP}_8}/\text{g-C}_3\text{N}_4$ also demonstrated recycling stability after hydrogenation process (Table S8 in the ESM). Furthermore, we investigated the catalytic activity of the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ for mutisubstituted benzaldehyde compounds, including p-hydroxybenzaldehyde, syringaldehyde, and isovanillin (Table 2). The experimental results showed that the catalyst had broad applicability for various substrates, such as lignin-derived aldehydes, and ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of catalytic products were provided in the ESM.

3.4 Photocatalytic mechanism

To verify the advantages of the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ catalyst in the catalytic reaction process, we studied the catalytic mechanisms through DFT calculations (Eqs. (S4)–(S7) in the ESM). Based on the above discussion, we propose a reasonable structure of $\text{Pd-Fe}_3\text{-N}_3$ for the reaction sites within the inner shell and conduct more detailed DFT calculations for this site (Fig. 5(f)). The vacancy formation energies of the reasonable configurations were compared to further demonstrate the stability of Pd–Fe coordination with different coordination numbers. The vacancy formation energies of Pd-Fe_1 , Pd-Fe_2 , and Pd-Fe_3 coordination were 1.59, 1.85, and 2.16 eV, respectively, which revealed that the Pd-Fe_3 coordination had the strongest lattice stability, as high coordination formed stronger metallic bonds, while low coordination was more prone to lattice distortion (Fig. 8(a)). Additionally, the high coordination number led to rearrangements of the charge in the specific orbitals of Pd, which directly affected the distribution of active sites on the inner shell, promoting catalytic activity for HDO of vanillin. Charge density difference was calculated to investigate the electron transfer in $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$. As shown in Fig. 8(b), the Pd atom was clearly identified as the positive charge center, indicating that electrons were directionally transferred from Pd to Fe atom in the Pd-Fe_3

Table 2 HDO of various substrates catalyzed by $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ ^a

Substrates	Products	Conv. (%) ^b	Yield (%) ^c
		83	76
		75	70
		85	81
		92	89
		93	89
		64	59
		94	90
		99	95
		99	96
		99	93
		72	64
		92	87

^aReaction conditions: vanillin (1 mmol), formic acid (2.5 mmol), photocatalyst (15 mg), solvent (H_2O , 6 mL; EA, 3 mL), 15 W LED with 413 nm, N_2 , and room temperature. ^bConversion was determined by HPLC. ^cIsolated yield.

coordination structure in the inner shell. Generally speaking, the electron transfer leads to a reduction in the electron filling of the Pd 3d orbitals and an upward shift of the d-band center, thereby enhancing the adsorption capacity for formic acid and vanillin. In addition, the electronic synergetic effect of Pd–Fe₃ coordination can timely regulate the charge at the metal interface during the catalytic reaction process to lower the activation energy barrier, as follows. The calculated density of states (DOS) of $\text{Pd}_{1+\text{NP}_8}/\text{g-C}_3\text{N}_4$ showed that the charge at the bottom of the valence band was mainly contributed by Pd, C, and N simultaneously, which was determined by the electron transfer in Pd–N coordination (Fig. 8(c)). As displayed in Fig. 8(d), DOS of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ revealed band gap contraction and the energy level contraction of Pd, due to the introduction of Fe and the electronic synergetic effect of Pd–Fe₃ coordination. Meanwhile, the fact that DOS of Pd did not cross the Fermi level indicated that it is dispersed in the form of single atoms, showing non-metallic properties. Besides, the partial DOS (PDOS) of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ showed that the d-band center of Pd was shifted upward due to the prominent contribution of the d_{z^2} orbital near the Fermi level, compared to that of $\text{Pd}_{1+\text{NP}_8}/\text{g-C}_3\text{N}_4$ (Fig. 8(e)).

Adsorption energies of two catalysts were calculated to evaluate the capacity for formic acid in the reaction process. The -1.07 eV of $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ showed a stronger adsorption capacity, which is attributed to the electronic synergy effect of the Pd–Fe₃ coordination, in comparison with -0.79 eV of $\text{Pd}_{1+\text{NP}_8}/\text{g-C}_3\text{N}_4$ (Fig. 8(f)). Adsorption energies for $-\text{OH}$, $-\text{OCH}_3$, and $-\text{CHO}$ groups of vanillin on the $\text{Pd}_1\text{Fe}_{20}/\text{g-C}_3\text{N}_4$ were calculated to precisely

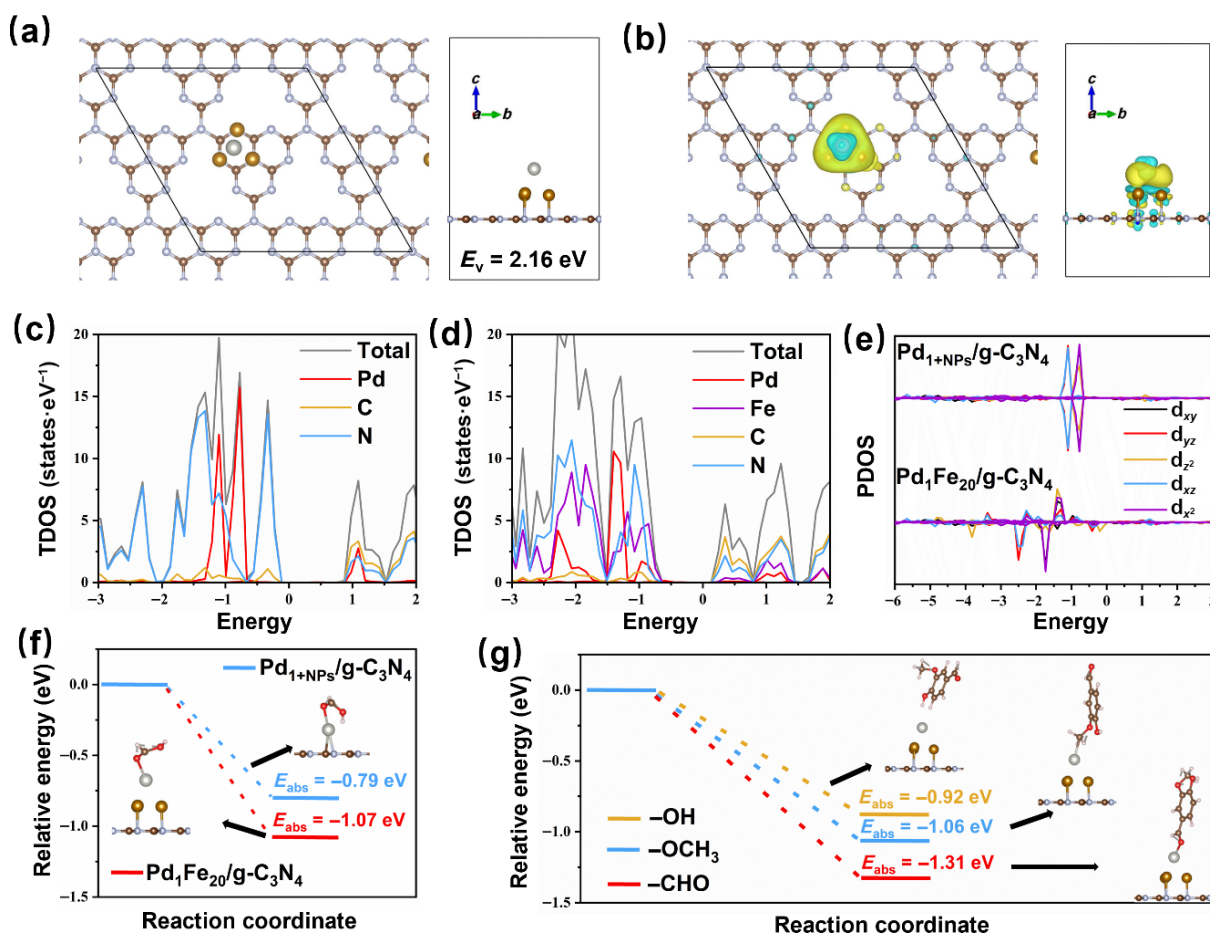


Figure 8 (a) Vacancy formation energy and (b) charge density difference of Pd-Fe₃ coordination. Density of states of (c) Pd_{1+NP9}/g-C₃N₄ and (d) Pd₁Fe₂₀/g-C₃N₄. (e) Partial density of states of Pd_{1+NP9}/g-C₃N₄ and Pd₁Fe₂₀/g-C₃N₄. (f) Adsorption capacity for formic acid. (g) Adsorption energy for -OH, -OCH₃, and -CHO of vanillin on the Pd₁Fe₂₀/g-C₃N₄.

delineate the reaction pathways. Obviously, the adsorption energy of -1.31 eV of Pd₁Fe₂₀/g-C₃N₄ for -CHO was the lowest, indicating that -CHO of vanillin preferentially adsorbed on the catalytic sites (Fig. 8(g)). Because the C=O of -CHO has strong coordination ability, which can form π anti-bonds with the d orbital of Pd, reducing the adsorption energy. Meanwhile, -OH groups are prone to form hydrogen bonds, while -OCH₃ groups have a relatively large steric hindrance. Generally, the atomic coordination environment of the catalyst will directly regulate the charge properties of the metal active sites and the adsorption capacity of the reactants. Especially, the electronic synergy effect of Pd-Fe₃ can significantly enhance the catalytic activity. Thus, the reaction energy barriers of the key steps were calculated to evaluate the influence of catalysts (Pd_{1+NP9}/g-C₃N₄ and Pd₁Fe₂₀/g-C₃N₄) with different coordination environments for the HDO process (Fig. 9(a)). The energy barriers for conversion of vanillin to HMP (transition states: TS1 and TS2) on Pd₁Fe₂₀/g-C₃N₄ were 0.62 and 0.26 eV, lower than those for Pd_{1+NP9}/g-C₃N₄, which were 1.07 and 0.3 eV, respectively. Further hydrogenolysis of HMP to MMP displayed energy barriers of 0.96 eV on Pd₁Fe₂₀/g-C₃N₄, significantly lower than 1.63 eV on Pd_{1+NP9}/g-C₃N₄. In addition, the energy barriers for conversion of HMP to MMP were significantly higher than process of vanillin to HMP on Pd_{1+NP9}/g-C₃N₄, which explained why only HMP was produced during the experiment (Table 1 and Table S6 in the ESM). This excellent catalytic performance was mainly attributed to the electronic synergetic effect of Pd-Fe₃ coordination in Pd₁Fe₂₀/

g-C₃N₄, which directs electron transfer and regulates catalytic activity of the Pd single atoms. Pd-Fe₃ coordination also promoted the release of free hydrogen from formic acid, leading to conversion of -CHO to -CH₃ on the Pd sites.

We investigated the adsorption behavior of different catalysts toward vanillin and HMP (Table S11 in the ESM). It revealed that Pd₁Fe₂₀/g-C₃N₄ has the best adsorption capacity for both vanillin and HMP compared to Pd_{1+NP9}/g-C₃N₄. Compared to vanillin, the adsorption capacity of Pd_{1+NP9}/g-C₃N₄ for HMP decreases, indicating that it is unfavorable for the subsequent reaction. This result further explains the reaction selectivity of different catalysts.

In addition, there should be more detailed discussions to verify the mechanism for HDO process of vanillin on the Pd₁Fe₂₀/g-C₃N₄ (Fig. 9(b)). As a hydrogen source, formic acid was adsorbed and interacted with the Pd active sites to form Pd-H species, which dominated the subsequent hydrogenation and hydrogenolysis processes. The carbon dioxide formed by formic acid dehydrogenation was absorbed by ethyl acetate to reduce the poisoning of Pd sites. During the hydrogenation of vanillin, the oxygen on the -CHO was preferentially adsorbed by Pd-H species, forming free hydrogen, which reacted with the oxygen to form -OH. Then, the carbon on the -CHO was adsorbed and hydrogenated, converting into HMP. Due to the difference in solubility, vanillin maintained a specific concentration in aqueous solution and participated in the hydrogenation with higher conversion ratio. During the hydrogenolysis, the oxygen and

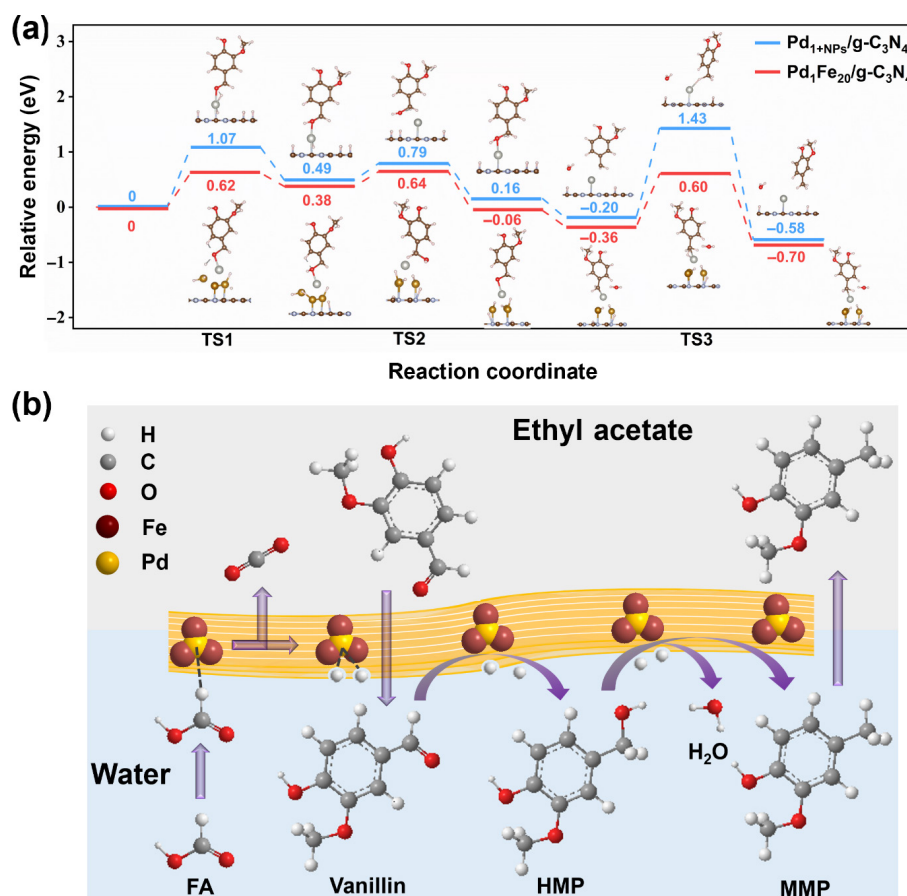


Figure 9 (a) Reaction pathway and free energy for $\text{Pd}_{1\text{Fe}_{20}}/\text{g-C}_3\text{N}_4$ in H₂O of vanillin. (b) The mechanism for HDO process of vanillin.

carbon atoms on the $-\text{CH}_2\text{OH}$ of HMP were adsorbed and reacted with free hydrogen to form MMP and release H₂O. MMP continuously concentrated in the ethyl acetate phase, maintaining a low concentration in aqueous solution and actively promoting the hydrogenolysis. As expected, the HDO of vanillin to MMP on the $\text{Pd}_{1\text{Fe}_{20}}/\text{g-C}_3\text{N}_4$ was perfectly demonstrated.

4 Conclusions

We have developed a photo-deposition strategy to controllably construct atomically dispersed Pd atoms through enhancing support's light absorption capacity for long wavelengths. The resulting $\text{Pd}_{1\text{Fe}_{20}}/\text{g-C}_3\text{N}_4$ catalyst was successfully prepared at 520 nm, where Pd existed only in the form of Pd^{2+} with loading of 0.24%. The light-driven HDO process on $\text{Pd}_{1\text{Fe}_{20}}/\text{g-C}_3\text{N}_4$ achieved 99% vanillin conversion and 99% MMP selectivity, and reached TOF of 2033 h^{-1} , which exceeded the literature reports. Pd single atoms and Pd-Fe₃ coordination were confirmed by XANES and EXAFS, which contributed to the catalytic performance. DFT studies further revealed the charge property of Pd atoms and the contribution of Pd-Fe₃ coordination to enhancing adsorption capacity for reactants and reducing the activation energy barrier. This strategy might address the issues of excessive use of precious metals, and provide ingenious ideas for the construction of single atom catalysts for biomass-derived conversions.

Electronic Supplementary Material: Supplementary material (preparation of photocatalysts; characterization methods; optical and electrochemical measurements; evaluation of photocatalytic

activity; equations of DFT calculations; tables of ICP-MS, and photocatalyst evaluation; figures of TEM, EDS, wavelet transform (WT)-EXAFS, and vacancy formation energy; and ¹H and ¹³C NMR spectra of catalytic products) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908845>.

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

Y. Y. W.: Data curation, validation, writing manuscript, experimental design. C. C.: Project administration, funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

None.

References

- [1] Zhang, B.; Biswal, B. K.; Zhang, J. J.; Balasubramanian, R. Hydrothermal treatment of biomass feedstocks for sustainable production of chemicals, fuels, and materials: Progress and perspectives. *Chem. Rev.* **2023**, *123*, 7193–7294.
- [2] Li, W.; Zhu, L. Y.; Xu, Y.; Wang, G. H.; Xu, T.; Si, C. L. Lignocellulose-mediated functionalization of liquid metals toward the frontiers of multifunctional materials. *Adv. Mater.* **2024**, *37*, 2415761.
- [3] Wang, Y. Y.; Cai, C. Photocatalytic oxidation of 5-hydroxymethylfurfural to selective products by noble metal-free Z-scheme heterostructures $\alpha\text{-Fe}_2\text{O}_3/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. *ACS Catal.* **2025**, *15*, 3451–3463.
- [4] Liu, W.; Liu, K.; Du, H. S.; Zheng, T.; Zhang, N.; Xu, T.; Pang, B.; Zhang, X. Y.; Si, C. L.; Zhang, K. Cellulose nanopaper: Fabrication, functionalization, and applications. *Nano-Micro Lett.* **2022**, *14*, 104.
- [5] Zhang, L. K.; Shang, N. Z.; Gao, S. T.; Wang, J. M.; Meng, T.; Du, C. C.; Shen, T. D.; Huang, J. Y.; Wu, Q. H.; Wang, H. J. et al. Atomically dispersed co catalyst for efficient hydrodeoxygenation of lignin-derived species and hydrogenation of nitroaromatics. *ACS Catal.* **2020**, *10*, 8672–8682.
- [6] Li, Z. J.; Lu, X. W.; Sun, W. W.; Leng, L. P.; Zhang, M. Y.; Li, H. H.; Bai, L.; Yuan, D. D.; Horton, J. H.; Xu, Q. et al. One-step synthesis of single palladium atoms in $\text{WO}_{2.72}$ with high efficiency in chemoselective hydrodeoxygenation of vanillin. *Appl. Catal. B: Environ.* **2021**, *298*, 120535.
- [7] Wang, X. C.; Arai, M.; Wu, Q. F.; Zhang, C.; Zhao, F. Y. Hydrodeoxygenation of lignin-derived phenolics—A review on the active sites of supported metal catalysts. *Green Chem.* **2020**, *22*, 8140–8168.
- [8] Yangcheng, R. X.; Ran, J. S.; Liu, Z. H.; Cui, Y. T.; Wang, J. J. Phosphoric acid-modified commercial kieselguhr supported palladium nanoparticles as efficient catalysts for low-temperature hydrodeoxygenation of lignin derivatives in water. *Green Chem.* **2022**, *24*, 1570–1577.
- [9] Yangcheng, R. X.; Li, J. W.; He, J. D.; Zheng, Y. X.; Yu, H. J.; Chen, C. L.; Wang, J. J. Carboxyl-decorated UiO-66 supporting Pd nanoparticles for efficient room-temperature hydrodeoxygenation of lignin derivatives. *Small* **2024**, *20*, 2309821.
- [10] Pu, C.; Zhang, J.; Zhang, G. G.; Xiao, Y. Y.; Ma, X. C.; Wu, J.; Luo, T. T.; Huang, K. X.; Ke, S. C.; Li, J. X. et al. Nitrogen precursor-mediated construction of N-doped hierarchically porous carbon-supported Pd catalysts with controllable morphology and composition. *Carbon* **2020**, *159*, 451–460.
- [11] Wu, J.; Liu, L. Q.; Yan, X. Y.; Wang, T. T.; Pan, G.; Bai, J. H.; Li, Y. Highly dispersed Pd nanoparticles immobilized on N-doped hollow carbon spheres for efficient catalytic hydrodeoxygenation of biomass-derived vanillin under atmospheric conditions. *ACS Sustain. Chem. Eng.* **2025**, *13*, 276–288.
- [12] Wang, L. H.; Zhang, H.; Chen, C. H.; Li, B.; Ning, H. H.; Lu, B.; Mao, S. J.; Wang, Y. Construction of molecularly dispersed polyoxometalate-alumina hybrid hollow nanoflowers via water-induced Kirkendall effect. *ACS Nano* **2024**, *18*, 24997–25008.
- [13] Qu, H. Y.; Hu, W. D.; Li, X. C.; Xu, R.; Han, X.; Li, J. J.; Lu, Y. Q.; Ye, Y. C.; Wang, C. M.; Wang, Z. et al. Efficient hydrogenolysis of 5-hydroxymethylfurfural to 2,5-dimethylfuran over $\text{Ni-C}_3\text{N}_4$ catalysts with ultra-low Ni loading. *Chin. J. Catal.* **2024**, *60*, 253–261.
- [14] Zhou, S. H.; Dai, F. L.; Dang, C.; Wang, M.; Liu, D. T.; Lu, F. C.; Qi, H. S. Scale-up biopolymer-chelated fabrication of cobalt nanoparticles encapsulated in N-enriched graphene shells for biofuel upgrade with formic acid. *Green Chem.* **2019**, *21*, 4732–4747.
- [15] Ge, F.; Liu, P.; Xu, W. L.; Jiang, J. C.; Zhou, M. H. Cobalt-glycerolates derived Co@C-T catalysts for the catalytic transfer hydrodeoxygenation of lignin-derived vanillin. *J. Colloid Interface Sci.* **2025**, *691*, 137444.
- [16] Gilkey, M. J.; Xu, B. J. Heterogeneous catalytic transfer hydrogenation as an effective pathway in biomass upgrading. *ACS Catal.* **2016**, *6*, 1420–1436.
- [17] Wu, P. Y.; Zhao, D. X.; Lu, G. P.; Cai, C. Supported Pd–Au bimetallic nanoparticles as an efficient catalyst for the hydrodeoxygenation of vanillin with formic acid at room temperature. *Green Chem.* **2022**, *24*, 1096–1102.
- [18] Verma, S.; Nasir Baig, R. B.; Nadagouda, M. N.; Varma, R. S. Visible light mediated upgrading of biomass to biofuel. *Green Chem.* **2016**, *18*, 1327–1331.
- [19] Liu, Y. N.; Meng, Q. L.; Zhang, K. L.; Han, W. Y.; Zheng, X. R.; Wang, Y. Q.; Han, Y. B.; Wang, J. P.; Wu, H. H.; He, M. Y. et al. Selective hydrogenation of phenols to cyclohexanones over hydrothermalite-supported Pd single-atom catalyst. *Angew. Chem., Int. Ed.* **2025**, *64*, e202504260.
- [20] Yan, Q.; Chen, Y.; Tang, B.; Wu, X.; Zhou, H.; Wang, H.; Li, H.; Lu, L. L.; Zhang, H.; Yang, S. et al. Precise engineering of asymmetric tri-active sites by symbiotic strategy for photocontrolled directional reforming of biomass. *Angew. Chem., Int. Ed.* **2025**, *64*, e202505718.
- [21] Chen, R. Z.; Chen, S. H.; Wang, L. Q.; Wang, D. S. Nanoscale metal particle modified single-atom catalyst: Synthesis, characterization, and application. *Adv. Mater.* **2024**, *36*, 2304713.
- [22] Li, X.; Liu, J. Q.; Wu, J. G.; Zhang, L. P.; Cao, D.; Cheng, D. J. Constructing a highly active Pd atomically dispersed catalyst for cinnamaldehyde hydrogenation: Synergistic catalysis between Pd–N₃ single atoms and fully exposed Pd clusters. *ACS Catal.* **2024**, *14*, 2369–2379.
- [23] Ouyang, Z. H.; Sheng, G.; Zhong, Y.; Wang, J.; Cai, J. X.; Deng, S. G.; Deng, Q. Palladium single atom-supported covalent organic frameworks for aqueous-phase hydrogenative hydrogenolysis of aromatic aldehydes via hydrogen heterolysis. *Angew. Chem., Int. Ed.* **2025**, *64*, e202418790.
- [24] Pang, T. R.; Xue, Z. L.; Wang, G. H.; Li, J. K.; Sui, W. J.; Si, C. L. Non-carbonized Pd single-atom catalyst supported on lignin-functionalized phenolic resin for potent catalytic transfer hydrogenation of lignin-derived aldehydes. *Angew. Chem., Int. Ed.* **2025**, *64*, e202503195.
- [25] Liu, P. X.; Zhao, Y.; Qin, R. X.; Mo, S. G.; Chen, G. X.; Gu, L.; Chevrier, D. M.; Zhang, P.; Guo, Q.; Zang, D. D. et al. Photochemical route for synthesizing atomically dispersed palladium catalysts. *Science* **2016**, *352*, 797–800.
- [26] Shi, Y. Z.; Luo, B. C.; Sang, R.; Cui, D. D.; Sun, Y.; Liu, R. Q.; Zhang, Z. L.; Sun, Y. F.; Junge, H.; Beller, M. et al. Combination of nanoparticles with single-metal sites synergistically boosts co-catalyzed formic acid dehydrogenation. *Nat. Commun.* **2024**, *15*, 8189.
- [27] Qi, H. F.; Li, Y. R.; Zhou, Z. T.; Cao, Y. Q.; Liu, F.; Guan, W. X.; Zhang, L. L.; Liu, X. Y.; Li, L.; Su, Y. et al. Synthesis of piperidines and pyridine from furfural over a surface single-atom alloy $\text{Ru}_1\text{Co}_{99}$ catalyst. *Nat. Commun.* **2023**, *14*, 6329.
- [28] Sun, Z. Y.; Li, C.; Lin, J.; Guo, T. Q.; Song, S. J.; Hu, Y. N.; Zhang, Z. D.; Yan, W. S.; Wang, Y.; Wei, Z. H. et al. Lattice strain and Mott–Schottky effect of the charge-asymmetry Pd_3Fe single-atom alloy catalyst for semi-hydrogenation of alkynes with high efficiency. *ACS Nano* **2024**, *18*, 13286–13297.
- [29] Liu, C. L.; Yang, R. Z.; Wang, J. C.; Liu, B. W.; Chang, X. W.; Feng, P. X.; Zhang, X. Z.; Zhong, L. J.; Zhao, X. L.; Niu, L. et al. Synergistic catalysts with Fe single atoms and Fe_3C clusters for accelerated oxygen adsorption kinetics in oxygen reduction reaction. *Angew. Chem., Int. Ed.* **2025**, *64*, e202501266.
- [30] Wang, Z. H.; Ding, Z.; Ali, A.; Tang, X. C.; Wang, J. K.; Sun, H. L.;

- Li, L. Y.; Tao, J. Z.; Chen, Z. X.; Cheng, L. et al. A dual strategy: Coordinating S-scheme heterostructure with single-atom sites for bifunctional photocatalysis. *Appl. Catal. B: Environ. Energy* **2026**, 387, 126466.
- [31] Qin, J. W.; Hu, Z. F.; Liu, Y. T.; Zhu, G. L.; Gan, Z. B.; Wang, C. C.; Zheng, X. W. Precise construction of carbon/nitrogen dual-defects synergizing with Co single-atoms for enhanced Fenton-like degradation of emerging contaminants. *Appl. Catal. B: Environ. Energy* **2026**, 386, 126432.
- [32] Zhao, Y. S.; Wan, J. W.; Ling, C. Y.; Wang, Y. L.; He, H. Y.; Yang, N. L.; Wen, R.; Zhang, Q. H.; Gu, L.; Yang, B. L. et al. Acidic oxygen reduction by single-atom Fe catalysts on curved supports. *Nature* **2025**, 644, 668–675.
- [33] Sheng, B.; Deng, C. Y.; Li, Y. F.; Xie, S. J.; Wang, Z. H.; Sheng, H.; Zhao, J. C. *In situ* hydroxylation of a single-atom iron catalyst for preferential $^1\text{O}_2$ production from H_2O_2 . *ACS Catal.* **2022**, 12, 14679–14688.
- [34] Ma, Z. M.; Liu, S. Q.; Tang, N. F.; Song, T.; Motokura, K.; Shen, Z. M.; Yang, Y. Coexistence of Fe nanoclusters boosting Fe single atoms to generate singlet oxygen for efficient aerobic oxidation of primary amines to imines. *ACS Catal.* **2022**, 12, 5595–5604.
- [35] Zhang, C.; Qin, D. Y.; Zhou, Y.; Qin, F. Z.; Wang, H.; Wang, W. J.; Yang, Y.; Zeng, G. M. Dual optimization approach to Mo single atom dispersed g- C_3N_4 photocatalyst: Morphology and defect evolution. *Appl. Catal. B: Environ.* **2022**, 303, 120904.
- [36] Zhao, E.; Kong, W. J.; Zoppellaro, G.; Yang, Y.; Nan, B.; Li, L. N.; Zhang, W. J.; Chen, Z. H.; Bakandritsos, A.; Wang, Z. J. et al. Atomic scale engineering of multivalence-state palladium photocatalyst for transfer hydrogenation with water as a proton source. *Adv. Mater.* **2025**, 37, 2504108.
- [37] Luo, L. H.; Wang, M. L.; Cui, Y.; Chen, Z. Y.; Wu, J. X.; Cao, Y. L.; Luo, J.; Dai, Y. Z.; Li, W. X.; Bao, J. et al. Surface iron species in palladium–iron intermetallic nanocrystals that promote and stabilize CO_2 methanation. *Angew. Chem., Int. Ed.* **2020**, 59, 14434–14442.
- [38] Zhong, H. X.; Ji, X. D.; Yang, C.; Tang, C. F.; Hu, X.; Cai, J. J.; Yin, Q.; Wang, J. J.; Hu, X. J.; Tan, X. F. et al. Z-scheme heterojunction $\alpha\text{-Fe}_2\text{O}_3$ /tubular g- C_3N_4 with C defects for photocatalytic degradation of microcystin-LR in water: Generation and effect of critical species $^1\text{O}_2$. *ACS Catal.* **2024**, 14, 6272–6291.
- [39] Zhang, H.; Wang, C. Q.; Luo, H. X.; Chen, J. L.; Kuang, M.; Yang, J. P. Iron nanoparticles protected by chainmail-structured graphene for durable electrocatalytic nitrate reduction to nitrogen. *Angew. Chem., Int. Ed.* **2023**, 62, e202217071.
- [40] Deng, P. L.; Xu, Y. S.; Wu, D. X.; Liang, Y.; Zhang, X.; Wang, Z. T.; Li, J.; Tian, X. L. Pd nanocatalysts engineering for direct oxidation methane-to-methanol with 99.7% selectivity. *Nat. Commun.* **2025**, 16, 7710.
- [41] Luo, L.; Fu, L.; Liu, H. F.; Xu, Y. X.; Xing, J. L.; Chang, C. R.; Yang, D. Y.; Tang, J. W. Synergy of Pd atoms and oxygen vacancies on In_2O_3 for methane conversion under visible light. *Nat. Commun.* **2022**, 13, 2930.
- [42] Lee, D. G.; Kim, D. H.; Lee, J. M.; Kim, B. J.; Kim, J. Y.; Shin, S. S.; Jung, H. S. High efficiency perovskite solar cells exceeding 22% via a photo-assisted two-step sequential deposition. *Adv. Funct. Mater.* **2021**, 31, 2006718.
- [43] Zhao, W. Y.; Song, S.; Ding, M. F.; Luo, W.; Li, L. D.; Li, X. G. Bypassing *in situ* CO poisoning in furfural conversion: Electron-deficient Pd single-atom alloys enable one-step selective synthesis of tetrahydrofuran. *Angew. Chem., Int. Ed.* **2025**, 64, e202507984.
- [44] Muthurasu, A.; Balaji, R.; Ko, T. H.; Kim, T. W.; Raj Rosyara, Y.; Kim, N. D.; Radhakrishnan, S.; Kim, H. Y. Atomically dispersed iron on functionalized boron nitride nanosheets for efficient oxygen reduction in proton exchange membrane fuel cells. *ACS Catal.* **2025**, 15, 18987–18994.
- [45] Ma, Y. L.; Pu, X.; Liu, Y. Q.; Zhou, P.; Han, X.; Ye, L.; Qin, X. L.; Xu, H. T.; Kong, L. T.; Li, J. B. et al. Synergistic catalysis over Pd–Fe–Zn with triple-interface structures for selective CO_2 hydrogenation to ethanol. *ACS Catal.* **2025**, 15, 18580–18590.
- [46] Luo, J.; Liu, Y. N.; Fan, C. Z.; Tang, L.; Yang, S. J.; Liu, M. L.; Wang, M. E.; Feng, C. Y.; Ouyang, X. L.; Wang, L. L. et al. Direct attack and indirect transfer mechanisms dominated by reactive oxygen species for photocatalytic H_2O_2 production on g- C_3N_4 possessing nitrogen vacancies. *ACS Catal.* **2021**, 11, 11440–11450.
- [47] Wang, Y. Y.; Cai, C. Composites of Fe_2O_3 quantum dots/2D g- C_3N_4 for heterogeneous photocatalytic oxidative trifluoromethylation of alkenes. *J. Catal.* **2025**, 451, 116385.
- [48] Geng, Y. X.; Chen, D. Y.; Li, N. J.; Xu, Q. F.; Li, H.; He, J. H.; Lu, J. M. Z-scheme 2D/2D $\alpha\text{-Fe}_2\text{O}_3$ /g- C_3N_4 heterojunction for photocatalytic oxidation of nitric oxide. *Appl. Catal. B: Environ.* **2021**, 280, 119409.



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