Synergistic Effect of Platinum Single Atoms and Nanoclusters Boosting Electrocatalytic Hydrogen Evolution

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Maximizing atomic utilization of precious metal-based catalysts is of great significance in heterogeneous catalysis, also becoming a useful strategy to develop efficient electrocatalysts for hydrogen evolution reaction (HER). Although the dispersion of platinum (Pt) as single atoms (SAs) has increasingly been used in the design of HER electrocatalysts, it is still controversial if the SAs possess higher reactivity relative to the nanoparticles with identical atom loading. Here, by virtue of computational studies, we find that atomic step-rich Pt clusters and defective graphene (DG)-loaded Pt SAs are beneficial to water dissociation and hydrogen coupling, respectively, predicting that decent activity and high atomic utilization for alkaline HER electrocatalysis will be exhibited on the structure that integrates both Pt SAs and nanoclusters onto the DG matrix (PtSA/NC-DG). We experimentally synthesize the PtSA/NC-DG catalyst for alkaline HER. The optimized PtSA/NC-DG delivers an overpotential of 41 mV at a current density of 10 mA cm\(^{-2}\) and mass activity of 5.4 mA μg\(^{-1}\) Pt at the overpotential of 100 mV. The mass activity is nearly 6 and 10 times higher than that of its Pt SA counterpart and commercial Pt/C catalyst. This work deepens the knowledge of the synergistic effect of single atoms and nanoclusters for alkaline HER electrocatalysis.

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### Introduction

Hydrogen production enabled by electrocatalytic methods represents an attractive approach to utilize renewable electricity from intermittent energy, such as solar, wind energy, geothermal power, and so forth. Although nonprecious materials based on earth’s abundant resources have achieved substantial development, platinum (Pt) is still the benchmark catalyst for the electrocatalytic hydrogen evolution reaction (HER) in terms of low overpotentials and high mass activities. The electrocatalytic hydrogen production in alkaline electrolytes offers more benign conditions compared with that of acid media. More importantly, alkaline water splitting into hydrogen allows the application of active catalysts based on earth-abundant transition metals for anodic oxygen evolution reaction. However, the catalytic activity of Pt in alkaline media is nearly two to three orders of magnitude slower than that in acid media due to the high-energy barrier of water dissociation. In terms of cost efficiency, it is highly desirable to reduce the Pt amount to the greatest extent, while maintaining or even improving catalytic activities.

In recent years, decreasing the size of catalytically active species in atomic dispersion, also referred to as single atoms (SAs), has attracted considerable attention thanks to their high atomic utilization and unique physicochemical properties. However, the catalytic nature remains highly controversial, especially since it is not clear how the SA sites achieve the splitting and recombination of chemical bonds. For instance, the hydrogen evolution process in alkaline media commonly consists of water dissociation and hydrogen coupling, a typical Volmer step ($\text{H}_2\text{O} + e^- \rightarrow \text{H}^+ + \text{OH}^- + \frac{1}{2} \text{H}_2$) and Heyrovsky step ($\text{H}_2\text{O} + \text{H}^+ + e^- \rightarrow \text{H}_2 + \text{OH}^- + \frac{1}{2} \text{H}_2$). The structure with dual active components, typically a metal/oxyde interfacial structure, has generally been adopted to optimize the water dissociation and hydrogen coupling simultaneously, boosting alkaline water electrolysis to produce hydrogen. To date, various attempts have successfully been made to obtain efficient low-Pt catalysts for acid HER electrocatalysis, but it has been determined that neither the Pt SAs nor nanoparticles deliver satisfactory performance in alkaline media. Developing efficient Pt-based catalysts with ultimate atomic utilization for alkaline HER electrocatalysis remains a severe challenge.

Here, we demonstrate both theoretically and experimentally that the synergistic function from the integration of defective graphene (DG)-supported Pt SAs and nanoclusters (named as PtSA/NC-DG) boosted electrocatalytic hydrogen evolution in alkaline media. In alkaline HER, given typical elementary steps of the water dissociation and hydrogen coupling, we employed density functional theory (DFT) calculations to compute the two steps onto Pt(111), Pt(211), Pt$_\text{SA}$ cluster, and DG-supported Pt SA models. It was revealed that the Pt nanoclusters and SAs helped water dissociation and hydrogen coupling, respectively. Therefore, the coexistence of Pt SAs and nanoclusters on the DG matrix would decouple the optimization of the two steps, integrally delivering superior hydrogen evolution. We experimentally synthesized the PtSA/NC-DG and DG-supported Pt SAs (named as PtSA-DG). The electrocatalytic performance of the PtSA/NC-DG outperformed that of PtSA-DG and commercial Pt/C catalysts, verifying the synergistic effect of Pt SAs and nanoclusters for alkaline HER electrocatalysis.

### Results and Discussion

#### Structural investigation by DFT calculation

The water dissociation and hydrogen coupling results on established models are shown in Figure 1 and
Supporting Information Table S1. It was found that the energy barrier of water dissociation ($E_{H2O}$) on a typical Pt(111) surface was estimated as 0.98 eV, and the hydrogen-binding energy ($\Delta G_{H*}$) was $-0.20$ eV, in keeping with previously published theoretical data.\textsuperscript{32,33} The results indicated the low activity of large size Pt crystals for alkaline HER electrocatalysis. When reducing the Pt size for the usage decrease, in addition to the thermodynamically stable Pt(111) surface, a high-index facet is increasingly exposed. Therefore, a typical high-index Pt(211) surface covered by atomic steps was here introduced.\textsuperscript{10} As shown in Figures 1a and 1b, the $E_{H2O}$ on the Pt(211) surface was 0.65 eV. On the contrary, the $\Delta G_{H*}$ ($-0.40$ eV) on the Pt(211) surface was extremely negative (Figures 1c and 1d). The results suggested that the atomic steps can accelerate water dissociation to supply $H^*$, but hamper the $H^*$ combination into $H_2$. It can reasonably be anticipated that atom-assembled nanoclusters with rich atomic steps can further facilitate the water dissociation, but severely hinder the hydrogen coupling. The computational $E_{H2O}$ and $\Delta G_{H*}$ on typical Pt$_{38}$ clusters were 0.59 and $-0.60$ eV, respectively, verifying that only the presence of nanoclusters can not efficiently accomplish the water splitting into $H_2$ (Figures 1b and 1d). In view of the ultimate in atomic utilization efficiency, Pt SAs anchored in suitable support naturally come to mind. Here, a nitrogen-doped defective carbon matrix for the anchoring of Pt SAs was considered, thanks to high structural feasibility and electronic conductivity as well as rich surface chemistry.\textsuperscript{34} Here, typical four-coordination structure is investigated in consideration of the high structure stability.\textsuperscript{10,32} It was determined that all simulated Pt$_x$C$_y$N$_z$ structures ($x + y = 4$) displayed large $E_{H2O}$ (Figure 1b), revealing the inferior water dissociation process. Moderate $|\Delta G_{H*}|$ was exhibited on most of the Pt$_x$C$_y$N$_z$ structures, including Pt$_3$C$_1$N$_3$, Pt$_2$C$_2$N$_2$, and Pt$_4$C$_4$ (Figure 1d), thereby benefitting the hydrogen coupling process on these structures. Combined with the aim of atomic utilization maximization, these theoretical results predicted that decent activity and high atomic utilization of alkaline HER electrocatalysis would be exhibited on the structure that integrates both Pt SAs and nanoclusters onto proper nitrogen-doped defective carbon support. In the integrated structure, Pt clusters can accelerate water dissociation to supply adsorbed $H$ atoms onto Pt clusters. The migration of $H$ atoms from Pt clusters to the graphene support and then to the SAs can be carried out through hydrogen spillover.\textsuperscript{35–37} The DG as the substrate of Pt clusters receives excess $H^*$ from the spillover. Most of Pt$_x$C$_y$N$_z$ structures are beneficial to the hydrogen coupling process.

![Figure 1](image-url)
Synthesis and characterization of DG-supported Pt catalysts

The nitrogen-doped DG selected for the loading of Pt species was obtained by the pyrolysis of the physical mixture of glucose and carbon nitride (Supporting Information Figures S1 and S2). Transmission electron microscopy (TEM) images showed typical graphene nanosheets with a high degree of structural wrinkle (Supporting Information Figure S3). The graphene displayed rich porosity and suitable pyridinic- or pyrrolic-nitrogen defects (Supporting Information Figures S4 and S5), which were beneficial to the anchoring of metal species. The Pt SAs were anchored onto the DG matrix by a one-step electroless deposition to obtain the PtSA-DG with 3.89 wt % Pt loading. Aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) images showed the Pt species of the PtSA-DG were atomically dispersed onto the DG support (Figure 2a and Supporting Information Figure S6). Subjected to thermal treatment at a different temperature, the PtSA-DG was transformed into the PtSA/NC-DG-X (X = 200, 400, or 600 °C). In the thermal treatment, a part of the Pt SAs owing to its unsaturated coordination structure and low binding energy with CN matrix (Pt-C$_x$N$_y$, $x+y<4$) were readily aggregated into Pt clusters. The Pt species in PtSA/NC-DG-X (X = 200, 400, or 600 °C) dispersed as Pt nanoclusters with a similar average diameter (Supporting Information Figure S7). Unless otherwise specified, the PtSA/NC-DG was the one obtained by heat treatment in 400 °C. From the HAADF-STEM images (Figure 2b and Supporting Information Figure S8), it was determined for the PtSA/NC-DG that both atom-assembled nanoclusters and SAs were dispersed onto the DG matrix. The energy-dispersive X-ray spectroscopy (EDS) mapping element further evidenced the coexistence of SAs and nanoclusters onto the nitrogen-doped carbon substrate (Figure 2c). X-ray diffraction (XRD) patterns (Figure 2d and Supporting Information S9) also revealed the presence and absence of crystalline Pt species in the PtSA/NC-DG and PtSA-DG, respectively.

X-ray absorption fine structure (XAFS) and X-ray photoelectron spectroscopy (XPS) measurements were carried out to identify the electronic and geometric structure of Pt species in the PtSA-DG and PtSA/NC-DG-X catalysts. The high-resolution Cl 2p XPS spectra showed the complete removal of chlorine (Supporting Information Figure S10), suggesting the absence of Pt-Cl coordination in the obtained catalysts. The normalized X-ray absorption near-edge structure (XANES) spectra showed that white-line intensity of all the PtSA-DG and PtSA/NC-DG-X catalysts was located among PtO$_2$ and Pt foil, demonstrating the existence of positively charged Pt species in these catalysts (Figure 3a). Furthermore, the decreased white-line intensity of PtSA/NC-DG-X catalysts indicated the enriching of Pt$^0$ species with the increase of annealing temperature, which was also evidenced by high-resolution Pt 4f XPS spectra (Supporting Information Figure S11). The coordination environments of Pt species were disclosed by

Figure 2 | Morphology and structure characterizations of PtSA-DG and PtSA/NC-DG. (a) High magnification HAADF-STEM image of PtSA-DG. (b) Gradually magnified HAADF-STEM images of PtSA/NC-DG. (c) Elemental mapping of PtSA/NC-DG. (d) XRD patterns of PtSA-DG and PtSA/NC-DG.

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k^3-weighted extended XAFS (EXAFS). From Figure 3b and Supporting Information Figure S12, it was clearly found that only the dominant peak of Pt-C/N/O coordination was observed for the PtSA-DG catalyst, confirming the atomic dispersion of Pt species. For the PtSA/NC-DG-X catalysts, in addition to the peak from Pt-C/N/O contribution, those peaks close to the Pt-Pt coordination were also observed, evidencing the coexistence of Pt SAs and nanoclusters, in line with the above HAADF-STEM results. To more directly discriminate the coordination environment of PtSA-DG and PtSA/NC-DG catalysts, an EXAFS wavelet transform (WT) was performed (Figure 3c). For the PtSA-DG catalyst, only one intensity maximum region close to that of PtO_2 was displayed, confirming the mononuclear centers of Pt species. Two maximum-intensity regions aligned with that of PtO_2 and Pt foil were observed for the PtSA/NC-DG catalyst, strongly evidencing the presence of Pt-C/N/O and Pt-Pt coordination. Combining these spectroscopic results with the above microscopic observation, it was demonstrated that the PtSA-DG and PtSA/NC-DG were successfully constructed.

**HER performance of different carbon-loaded Pt catalysts**

The high-performance catalytic activities of the PtSA/NC-DG for alkaline HER were verified in a typical three-electrode cell filled by 1 M KOH. First, from the polarization curves of PtSA/NC-DG-X catalysts (Supporting Information Figure S13), the PtSA/NC-DG obtained at 400 °C was reactivity-optimized, probably due to the suitable ratio of Pt SAs and nanoclusters. The optimized PtSA/NC-DG achieved an overpotential (Ω) of 41 mV at a current density of 10 mA cm\(^{-2}\), significantly surpassing that of the PtSA-DG and commercial 20 wt % Pt/C catalysts (Figure 4a and Supporting Information Figure S14). The comparison of mass activities for precious metal-based catalysts is of great importance. Thus, the mass activities of PtSA-DG, PtSA/NC-DG, and commercial Pt/C were calculated based on the Pt loading at the electrode. The PtSA/NC-DG delivered significantly higher mass activity than the PtSA-DG and commercial Pt/C (Figure 4b and Supporting Information Figure S15). In particular, the mass activity of PtSA/NC-DG was as high as 5.40 mA µg\(^{-1}\) at 100 mV, which was nearly 6 and 10 times higher than that of PtSA-DG (0.83 mA µg\(^{-1}\)) and commercial Pt/C (0.52 mA µg\(^{-1}\)). In addition, the calculated turnover frequency (TOF) also demonstrated the remarkable activity of the PtSA/NC-DG (Supporting Information Figure S16). From Supporting Information Figure S17, the Tafel slope of PtSA/NC-DG (40 mV dec\(^{-1}\)) was close to that of commercial Pt/C, and was lower than that of PtSA-DG, following the Volmer–Tafel mechanism. Moreover, the exchange current density of PtSA/NC-DG was 1.25 mA cm\(^{-2}\) (Figure 4c), which is nearly seven and two times larger than that of PtSA-DG and commercial Pt/C, indicating rapid reaction kinetics of the PtSA/NC-DG. To further compare the intrinsic activity, the electrochemically
active surface area (ECSA) was evaluated (Supporting Information Figure S18). The ECSA-normalized mass activity of the PtSA/NC-DG at 100 mV was still five times higher than that of the PtSA-DG (Supporting Information Figure S19), demonstrating superior intrinsic activity. To rule out the possible influence of particle size, exposed surface and the metal–support interaction, we prepared the Pt nanoclusters supported on high-surface-area carbon black support (PtNC-BP2000-400) with similar Pt loading according to previous studies. The PtNC-BP2000-400 without Pt SAs displayed a similar size of Pt clusters with PtSA/NC-DG (Supporting Information Figure S20), which was also confirmed by high-resolution Pt 4f XPS spectra (Supporting Information Figure S21). The metal–support interaction result from particle size could also be excluded. Then, we compared their electrocatalytic activity and stability. The PtSA/NC-DG catalyst displayed a lower overpotential and superior stability than PtNC-BP2000-400 (Supporting Information Figure S22). The negligible overpotential increase after accelerated degradation test evidenced the long-term stability of PtSA-DG and PtSA/NC-DG, probably thanks to the confinement effect of the defective carbon matrix (Figure 4d and Supporting Information Figures S23 and S24). HAADF-STEM images of PtSA/NC-DG after 10,000 cycles further confirmed that PtSA/NC-DG is only slight larger than that of slight larger than that of the pristine PtSA/NC-DG (Supporting Information Figure S25). N 1s and Pt 4f high-resolution XPS spectrum of PtSA/NC-DG further demonstrated the outstanding structural stability of PtSA/NC-DG catalyst (Supporting Information Figures S26 and S27). The PtSA/NC-DG compared with that of PtSA-DG, PtNC-BP2000-400, commercial Pt/C as well as other Pt-based catalysts (Supporting Information Table S2) displayed higher activity, verified the above theoretical synergistic effect of Pt SAs and nanoclusters boosting water splitting into hydrogen.

Conclusion

Combining the DFT simulation and experimental verification, we have reported a highly efficient PtSA/NC-DG electrocatalyst for alkaline HER by the integration of Pt nanoclusters and SAs onto DG matrix. In the integrated structure, the Pt nanoclusters promote water dissociation into *H and *OH, and the Pt SAs facilitate the H–H coupling into gaseous hydrogen. Consequently, despite low Pt loading in the PtSA/NC-DG catalyst, the electrocatalytic performance toward alkaline HER is

Figure 4 | Electrochemical characterization. All data are IR-corrected. (a) LSV curves of PtSA-DG, PtSA/NC-DG, and commercial Pt/C in 1 M KOH. (b) Mass activities of PtSA-DG, PtSA/NC-DG, and commercial Pt/C at an overpotential of 50 and 100 mV. (c) Exchange current density of PtSA-DG, PtSA/NC-DG, and commercial Pt/C. (d) LSV curves of PtSA/NC-DG recorded initially and after 10,000 potential cycles. IR, infrared; LSV, linear sweep voltammetry.
substantially better than that of the Pt SA counterpart and commercial Pt/C catalyst with 20 wt % Pt. The notion presented in this work will provide some guidance for the design of noble metal-based heterogeneous catalysts approaching the ultimate in atomic utilization efficiency.

Supporting Information

Supporting Information is available.

Conflict of Interest

There is no conflict of interest to report.

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