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Encapsulating Pt Nanoparticles inside a Derived 2D Metal-Organic Frameworks for the Enhancement of Catalytic Activity

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ABSTRACT:

The development of highly active and stable electrocatalysts towards oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) are key for commercial application of fuel cells and water-splitting. Here we report a highly active and stable Pt nanoparticles (NPs) encapsulated in the ultrathin 2D carbon layers derived from the ultrathin 2D MOF precursor (ZIF-67). Electrochemical tests reveal that our approach not only successfully stabilized Pt NPs but also boosted Pt activities towards ORR and HER. We found that our Pt catalysts encapsulated in the ultrathin 2D carbon layers exhibited an ORR activity 5.9 and 12 times greater than that of the commercial Pt/C and Pt/RGO without 2D carbon layers protection, respectively. Our encapsulated Pt catalysts also show more than 9 times more stable than that of Pt/C catalyst. In addition to ORR, our novel encapsulated Pt catalysts display an extraordinary stability and activity towards the HER with lower overpotential (14.3 mV in acid media and 37.2 mV in alkaline media) at the current density of 10 mA cm$^{-2}$ compared with Pt/C catalyst (23.1 mV in acid media and 92.1 mV in alkaline media). The enhanced electrochemical activities and stability of our encapsulated Pt catalysts are attributed to the synergetic effect of Pt-based NPs and ultrathin 2D carbon layers derived from ZIF-67 with enriched in active sites of Co-N$_{x}$. First-principles simulations reveal that the synergistic catalysis of Pt-based NPs and Co-N$_{x}$ derived from ZIF-67 improve the activity for ORR and HER.
# Introduction

Platinum (Pt)-based catalysts are believed as the most efficient electrocatalysts in many important clean energy processes such as hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in fuel cells, and hydrogen evolution reaction (HER) in electrochemical water splitting.\(^1\)-\(^6\) To maximize the Pt utilization efficiency and decrease the cost of catalysts, Pt nanoparticles (NPs) or clusters, even atoms were deposited on a support to improve the catalytic performance. However, the instability is still one of the major challenges for supported Pt NPs in practical applications because NPs to easily aggregate and form larger particles to minimize the surface energy, resulting in a serious loss of the catalytic activity.\(^7\)-\(^9\) Moreover, supported Pt NPs often suffer from performance degradation due to the dissolution, detachment, or aggregation of Pt NPs on supports in harsh environments such as high potential, concentrated acid and alkaline media in practical applications.\(^2,\)\(^10\)-\(^11\)

To address the above challenges associated with supported Pt catalysts, one of the best strategies is surface protection of individual metal nanoparticles encapsulated into an ultrathin layer, which can effectively suppress the leaching, detachment and agglomeration of metal NPs on supports, leading to the enhancement of activity and stability of metal NPs.\(^10\) So far, various protective layers such as carbon,\(^12\)-\(^14\) metal oxides,\(^15\)-\(^17\) and polymers\(^18\)-\(^19\) have been utilized to stabilize NPs, which show enhanced stability in comparison with the unprotected counterparts. Especially, it is known that carbon layers are the good protective layers to stabilize the small NPs due to the high conductivity and excellent chemical stability in acid and alkaline media. The encapsulated NPs with carbon layers\(^12,\)\(^20\)-\(^21\) exhibited an enhanced stability in comparison with unprotected NPs catalysts because carbon layers can not only inhibit NPs from migrating, agglomerating and detaching, but also alleviate the leaching of NPs dissolution. N-doped carbon layers\(^14,\)\(^22\)-\(^23\) also
were used as protective layers to stabilize the metal NPs, which increase the activity in addition to the enhancement in the stability due to the N-C also acts as an active site.

The precise controlled thickness of protective layers play a vital role in the performance of the surface protection of individual metal nanoparticles because too thin layers cannot effectively protect the metal NPs while too thick ones lead to a decrease in catalytic activity resulting from mass transfer resistance. In addition, the precise structure design of the protective layers such as nanopore, nanobowl, nanocage and nanotrap with open nanochannels is crucial for high activity of encapsulated metal NPs because those nanochannels could not only highly expose the active sites, but also facilitate the mass transfer for the reactants and products and eliminate the deactivation of catalysts by lowering the diffusion. Recently, Metal-Organic Frameworks (MOFs) have been indicating promising potentials to become a new generation of protective layer materials for encapsulating NPs because cavities in MOFs could favor the mass transfer in comparison with conventional porous materials. The most reported method to encapsulate metal NPs into MOFs is growth of the granular MOFs crystals shell on the surface of metal NPs through mixing MOFs precursors of both metal ions and organic linkers, however, the precise control of the shell thickness and open nanochannels of MOFs layers is still a challenge. Besides the challenges associated with instability of Pt catalysts, another major problem for Pt electrocatalysts is high cost due to expensive and scarce of Pt. Therefore, it is extremely desirable to further improve the activity and stability of the Pt-based catalysts for their widespread application.

In this work, taking the advantage of MOFs, we propose a strategy to design highly active and stable catalysts through encapsulating Pt NPs in ultrathin 2D cobalt MOFs (ZIF-67)-derived carbon layers. The precise control of ultrathin 2D carbon layers plays a vital role in achieving high
active and stable encapsulated Pt catalysts, in which ultrathin 2D carbon layers not only suppress
the growth and leaching of metal NPs resulting in high stability, but also solve the diffusion
barriers for the reactants and products without lowering the activity of catalysts. An outline of the
synthetic strategy for the Pt encapsulated in ultrathin 2D carbon layers is illustrated in Scheme 1.
The uniform Pt NPs were firstly deposited on the graphene oxides and then the ultrathin 2D ZIF-
67 using 2-methylimidazole and cobalt (II) nitrate hexahydrate as precursors grew around Pt NPs
on the surface of GO. In this work, we precisely control the thickness of the ultrathin 2D MOFs
through step-by-step method. After thermal decomposition of ultrathin 2D ZIF-67 precursors,
the Pt NPs encapsulated in ultrathin 2D carbon layers derived from ZIF-67 precursors show high
stability with enhanced activity towards ORR and HER due to the synergistic effect between Pt
catalysts and the active sites (Co-Nₓ) on ZIF-67 derived ultrathin 2D carbon layers.

Scheme 1. Schematic of the Strategy for the synthesis of Pt NPs encapsulated in ultrathin 2D
carbon layers derived from ultrathin 2D MOFs layers.

Results and discussion
The GO was regarded as a good adsorption material for heavy metal ions due to their excellent adsorption performance. The GO can effectively bind a metal ion through sharing an electron pair resulting from the carbonxylate groups such as -COOH, -C=O. Taking advantage of the excellent adsorption performance of graphene oxide, cobalt ions could be anchored to the GO surface through the strongly coordination of carboxylate groups with metal cations, and subsequently form 2D MOFs by assembled adsorbed metal cations with organic linkers. In order to precisely control the thickness of 2D ZIF-67, we adopted the step-by-step method to grow 2D ZIF-67 on the surface of GO. The typical procedure includes the following steps: (1) the adsorption of cobalt ions on the GO in methanol solution; (2) the collection of graphene oxides adsorbed cobalt ions through removal of the excess cobalt precursor in solution; (3) the reaction of 2-methylimidazole with cobalt ion adsorbed to form ZIF-67 on graphene oxides; (4) the collection of the mixture of ZIF-67 on graphene oxides by removing the excess 2-methylimidazole. One cycle of growth of ZIF-67 layers on GO was achieved. Through tuning the number of the above procedure, the thickness of 2D ZIF-67 on GO can be precisely controlled. We firstly investigated the thickness of porous N-doped carbon layers derived from ZIF-67 on GO by atomic force microscope (AFM). As shown in Figure S1, the thickness of porous N-doped carbon layers derived from 1 cycle ZIF-67 coated GO is about 1.8 nm. The thickness of porous N-doped carbon layers derived from ZIF-67 increased with the increase in cycles of ZIF-67 coated GO. The thickness of carbon layers derived from 3 and 5 cycle ZIF-67 coated GO were about 4.0 nm and 5.7 nm, respectively.

To avoid destroying the nature of oxygen-containing functional groups on GO, we firstly prepared Pt NPs using a modified polyol method, followed by depositing Pt NPs on GO at
Figure 1. The high-TEM image of (a) 3ZIF-67-Pt/RGO and (b) 5ZIF-67-Pt/RGO treated at 600°C for 3h at N₂ atmosphere. (c) EDX mapping of 3ZIF-67-Pt/RGO.

room temperature. The Pt NPs with average particle size of 2.1 nm in a diameter were uniformly supported on the surface of GO (Figure S2). As shown in Scheme 1, the Pt encapsulated in the ultrathin 2D ZIF-67 formed by growth of ZIF-67 around Pt on the surface of GO. After the
pyrolysis of Pt encapsulated in ultrathin 2D MOFs layers, we found that the ultrathin 2D carbon layers as protective layers can effectively prevent Pt sintering and aggregation. As shown in Figure S3, the average size of Pt NPs on graphene without MOF protective layers show a distinct aggregation and increased from 2.1 nm to 5.3 nm with large size range annealing at 600°C for 3 h at N₂ atmosphere. In contrast, the average size of Pt NPs with 1 cycle ZIF-67 protective layer increased to 4.2 nm (Figure S3b). The average size of Pt NPs in a diameter increased slightly to 3.1 and 2.9 nm for 3ZIF-67-Pt/RGO and 5ZIF-67-Pt/RGO, respectively (Figure 1 and Figure S3). More importantly, we found that the thickness of ultrathin carbon layers derived from ZIF-67 increase with the cycle. For the 1ZIF-67-Pt/RGO, the carbon layers were not clearly observed because the thickness was too thin. It is obvious that ultrathin carbon layers derived from ZIF-67 formed around the Pt NPs for 3ZIF-67-Pt/RGO (Figure 1a). The thickness of the carbon layers of 5ZIF-67-Pt/RGO is higher than that of 3ZIF-67-Pt/RGO. However, compared with 3ZIF-67-Pt/RGO, it is observed that some Pt surface covered by the derived carbon layers for 5ZIF-67-Pt/RGO resulting from the higher thickness of ZIF-67 and epitaxial growth (Figure 1b). Those covered Pt surface may result in the loss of activity due to the blocking Pt active site covered by protective layers. The energy-dispersive X-ray spectroscopy (EDS) mapping reveals elements Pt, Co, and N were homogeneously distributed in 3ZIF-67-Pt/RGO (Figure 1c). In addition, some Pt₃Co NPs were observed in 3ZIF-67-Pt/RGO and 5ZIF-67-Pt/RGO due to the incorporation of the Co into the Pt NPs at high temperature, which is proved to improve the activity of Pt NPs. The stabilization effect of MOF protective layers for Pt NPs was further confirmed by X-ray diffraction (XRD) as shown in the Figure 2a, which showed broader peaks for Pt NPs encapsulated in ultrathin 2D carbon layers in compared with Pt/RGO without carbon protective layers. In addition, the XRD showed that the Pt/RGO is typical face-centred cubic (fcc) structure. Compared
Figure 2. (a) XRD patterns and (b) XPS Pt 4f spectra of Pt/RGO and Pt/RGO with different cycles ZIF-67.

with the Pt/RGO, the ZIF-67-Pt/RGO show Pt-Co peak in addition to the Pt peak, indicating that partial Pt NPs gradually convert to Pt-Co alloy through the incorporation of the Co into the Pt fcc structure at high temperature.\textsuperscript{45} The Pt alloyed with transition metals is proved to enhance the Pt activity.\textsuperscript{46-47} The X-ray photoelectron spectroscopy (XPS) further confirmed this transformation from partial Pt NPs to Pt-Co alloy. As shown in Figure 2b, the deconvolution of Pt 4f spectrum indicates four peaks which located at about 70.9 and 74.2 eV assigned to the 4f\textsubscript{7/2} and 4f\textsubscript{5/2} of metallic Pt; 71.9 and 75.3 eV attributed to the 4f\textsubscript{7/2} and 4f\textsubscript{5/2} of Pt\textsuperscript{2+}. As shown in Table 1, the Pt 4f binding energy of 3ZIF-67-Pt/RGO and 5ZIF-67-Pt/RGO shows a \sim0.4\ eV positive energy shift in comparison with the Pt/RGO, resulting from the formation of Pt-Co alloy.\textsuperscript{43} Three types of nitrogen species for 5ZIF-67-Pt/RGO sample could be observed in the high-resolution XPS N 1s spectra (Figure S5a): pyridinic-N (\sim398.3\ eV), graphitic-N (\sim401.0\ eV) and Co-N\textsubscript{x} (\sim399.5\ eV).\textsuperscript{48} In addition to cobalt, the Co XPS further shows that the cobalt exist as Co-N\textsubscript{x} in 5ZIF-67-Pt/RGO (Figure S5b).\textsuperscript{49-50} This finding is in according with the previous studies which showed the formation of Co-N\textsubscript{x} species in ZIF-67 derived carbon nanomaterials.\textsuperscript{51-52} XPS did not detect
the cobalt signal because of low content of cobalt in 1ZIF-67-Pt/RGO and 3ZIF-67-Pt/RGO (Figure S4).

We first investigate the effect of different ZIF-67 growth cycle on the electrochemical active surface area (ECSA) and ORR activity of encapsulated Pt NPs. As shown in Figure S6, the ECSA of 3ZIF-67-Pt/RGO is measured to be 55.8 m\(^2\)g\(^{-1}\), which is larger than that of 1ZIF-67-Pt/RGO (36.1 m\(^2\)g\(^{-1}\)) and 5ZIF-67-Pt/RGO (46.7 m\(^2\)g\(^{-1}\)). Compared with 3ZIF-67-Pt/RGO, 5ZIF-67-Pt/RGO has lower ECSA due to the larger size of Pt NPs, which is in good agreement with the result of TEM (Figure S3 and Figure 1). The lower ECSA on 5ZIF-67-Pt/RGO is should be attributed to some Pt surface covered by ZIF-67, in according to the observation from the TEM (Figure 1). This finding suggests that it is very important to control the cycle of ZIF-67 for high performance of Pt NPs encapsulated in ultrathin 2D carbon layers derived from ZIF-67. According to ORR polarization curves in Figure 3, the ORR activity of different catalysts increases in the order Pt/RGO < 1ZIF-67-Pt/RGO < Pt/C < 5ZIF-67-Pt/RGO < 3ZIF-67-Pt/RGO in terms of the half-wave potential. Pt/RGO has lowest ORR activity because of large Pt particles resulting in treated in high temperature. 3ZIF-67-Pt/RGO has higher ORR activity than the 5ZIF-67-Pt/RGO (Figure 3a), which mainly because some Pt surface covered by the carbon layers derived from the ZIF-67 in 5ZIF-67-Pt/RGO (Figure 1b). Those ORR performance is in consist with the analysis of TEM images. So it is very important to optimize the structure of the protecting layers for encapsulated metal NPs, which will lead to highest exposed active site of NPs and promote the mass transfer.\(^{15}\) As shown in Figure 3b, the mass activity of 3ZIF-67-Pt/RGO is 208 mA·mg\(^{-1}\), which is 5.9 times and 12 times better than that of commercial Pt/C catalyst (35 mA·mg\(^{-1}\)) and Pt/RGO (17 mA·mg\(^{-1}\)), respectively. The 3ZIF-67-Pt/RGO catalyst also show higher ORR activity than that the PtCo alloy prepared by typical wet chemical method (Figure S7a). In addition, the
3ZIF-67-Pt/RGO catalyst indicates higher ORR activity than that of Pt NPs encapsulated in the ultrathin 2D carbon layers derived from the 3cycles of ZIF-8 precursors (Figure S7b). Besides, carbonized ZIF-67 on GO without Pt NPs shows poor ORR activity (Figure S7c). So, the enhanced

![Figure 3](image)

**Figure 3.** (a) ORR polarization curves for Pt/C, Pt/RGO and Pt/RGO with different cycles ZIF-67 in O₂-saturated 0.5M H₂SO₄ at room temperature, with rotation rate of 1,600 rpm. and sweep rate, 10 mV s⁻¹. (b) Mass activity at 0.9 V (vs RHE) for Pt/C, Pt/RGO and Pt/RGO with different cycles ZIF-67 before and after ADT. (c) Durability tests for 3ZIF-67-Pt/RGO in O₂-saturated 0.5M H₂SO₄ solution at room temperature. (d) HRTEM image of 3ZIF-67-Pt/RGO after ADT.
ORR activity is probably due to the synergistic catalysis of Pt-based NPs and Co-N$_x$ derived from ZIF-67. \(^{53-54}\) As reported, the Co-N$_x$ derived from ZIF-67 has been widely recognized as active sites for ORR in both acidic and alkaline solutions. \(^{55-56}\) The accelerated durability tests (ADT) were conducted to study the effect of stabilization of ultrathin carbon layers derived from ZIF-67 using cycling the potentials between 0.6 and 1.0 V \textit{vs.} RHE in 0.5M H$_2$SO$_4$ using RDE. It was reported that the performance degradation of supported Pt NPs results from the dissolution, migration and agglomeration of NPs in the cycling potential range between 0.6 and 1.0 V \textit{vs.} RHE. \(^{46}\) As shown in \textbf{Figure 3b-c} and \textbf{Figure S8}, ultrathin carbon layers derived from ZIF-67 can effectively enhance the stability of Pt NPs. After ADT, 3ZIF-67-Pt/RGO and 5ZIF-67-Pt/RGO catalysts lost only about 7% and 5% of their initial Pt ORR mass activities respectively, while Pt/C and Pt/RGO catalyst decreased by 46% and 40% of their initial mass activities, respectively. After 10000 cycles, the mass activity of 3ZIF-67-Pt/RGO is 193 mA·mg$^{-1}$, which is more than 10 time higher than that of Pt/C catalyst (19 mA·mg$^{-1}$). No significant aggregation or morphology change was observed for the 3ZIF-67-Pt/RGO catalyst, generally maintaining its initial size of Pt NPs after long-term potential cycling (\textbf{Figure 3d} and \textbf{Figure S9}), while the size of the Pt NPs in the Pt/C catalyst significantly increased from 3.6 nm to 7.8 nm as shown in \textbf{Figure S10}. This finding suggested that the 2D ultrathin carbon layers derived from ZIF-67 can effectively stabilize the encapsulated Pt NPs and protect Pt NPs from agglomeration and coarsening.

We also investigated the HER electrocatalytic activity of Pt catalysts encapsulated in ultrathin 2D ZIF-67 layers using RDE in acid solution. The Pt NPs encapsulated in ultrathin 2D ZIF-67 layers clearly show better HER activities than the Pt/C and Pt/RGO catalysts in acid solution (\textbf{Figure 4a}). At the current density of 10 mA cm$^{-2}$, the 3ZIF-67-Pt/RGO has a lowest overpotential of 14.3 mV while 1ZIF-67-Pt/RGO and 5ZIF-67-Pt/RGO showed an overpotential of 18.2 mV and
16.5 mV, respectively, which are much lower than that of commercial Pt/C (23.1 mV) and Pt/RGO (29.0 mV) at same Pt loading (Figure 4b). In addition, 3ZIF-67-Pt/RGO showed better HER activity in comparison with PtCo alloy prepared by wet method (Figure S12a). The Tafel plots and electrochemical impedance spectroscopy (EIS) were further used to gain insight into the high HER catalytic performance of 3ZIF-67-Pt/RGO. The 3ZIF-67-Pt/RGO has smallest Tafel slope of 12.5 mV dec\(^{-1}\) (Figure S11a), which is faster than those of 5ZIF-67-Pt/RGO (13.6 mV dec\(^{-1}\)), 1ZIF-67-Pt/RGO (13.7 mV dec\(^{-1}\)), Pt/C (17.3 mV dec\(^{-1}\)) and Pt/RGO (18.2 mV dec\(^{-1}\)) catalysts, displaying more favorable HER catalytic kinetics on the 3ZIF-67-Pt/RGO in acid solution. As displayed in Figure S11b, the 3ZIF-67-Pt/RGO was observed to have smallest charge-transfer resistance among all samples, indicating 3ZIF-67-Pt/RGO possesses stronger charge transfer ability during HER process in acid electrolyte. ADT were adopted to evaluate the durability of the as-prepared catalysts. The 3ZIF-67-Pt/RGO demonstrated significantly higher HER stability compared to the commercial Pt/C (Figure 4c and Figure S12b).

We further studied the HER activity of as-prepared catalysts in alkaline media which is a major challenge for Pt catalyst because the alkaline HER activity of Pt catalysts is about 2-3 orders of magnitude lower than that in acidic media. \(^{57}\) As shown in the Figure 4d and e, the Pt/C catalyst shows lower HER activity with an overpotential of 92.1 mV in the alkaline solution. It is surprise that the Pt NPs encapsulated in 2D ultrathin carbon layers derived from ZIF-67 indicate enhanced HER activity in alkaline media. The 3ZIF-67-Pt/RGO and 5ZIF-67-Pt/RGO catalysts show an overpotential of 37.2 mV and 48.4 mV, respectively, which are much lower than that of commercial Pt/C (92.1 mV). The excellent HER activity on 3ZIF-67-Pt/RGO sample is also reflected by the Tafel slope and EIS measurement in alkaline media as shown in Figure S11c and d. The 3ZIF-67-Pt/RGO shows smaller Tafel slope and charge-transfer resistance. In addition,
Figure 4. (a) Polarization curves and (b) overpotential at 10 mA cm$^{-2}$ of Pt/C, Pt/RGO and Pt/RGO with different cycles ZIF-67 in 0.5M H$_2$SO$_4$ at a scan rate of 5 mV·s$^{-1}$ with rotation rate of 1,600 rpm. (c) Polarization curves recorded for 3ZIF-67-Pt/RGO before and after 1000 CV cycles in 0.5M H$_2$SO$_4$ (cycling sweep range: -0.04 V to 0.36 V vs RHE). (d) Polarization curves and (e) Overpotential at 10 mA cm$^{-2}$ of Pt/C, Pt/RGO and Pt/RGO with different cycles ZIF-67 in 1M KOH at a scan rate of 5 mV·s$^{-1}$ with rotation rate of 1,600 rpm. (f) Polarization curves recorded for 3ZIF-67-Pt/RGO before and after 1000 CV cycles in 1M KOH (cycling sweep range: -0.15 V to 0.25 V vs RHE).
3ZIF-67-Pt/RGO also showed higher HER activity than PtCo alloy prepared by wet method (Figure S12c). After the durability tests, the 3ZIF-67-Pt/RGO retained a similar performance to the initial HER activity, demonstrating significantly higher HER stability compared with the commercial Pt/C in alkaline media (Figure 4f and Figure S12d). In addition, the carbonized ZIF-67 on GO without Pt NPs indicates low HER activity in acid and alkaline media (Figure S13). Those findings suggested that the excellent catalytic activity and stability of 3ZIF-67-Pt/RGO in acid and alkaline media. The enhanced HER performance of 3ZIF-67-Pt/RGO is probably due to the unique structure of Pt encapsulated in ultrathin 2D carbon layers. The ultrathin 2D carbon protective layers derived from ZIF-67 is responsible for those remarkable improvement in the stability. The synergistic catalysis of Pt-based NPs and Co-N\textsubscript{x} \textsuperscript{58-60} derived from ZIF-67 can improve the HER activity in both acid and alkaline media.

We performed DFT calculations to further understand the synergistic effects between the Co-N\textsubscript{x} and Pt NPs during electrocatalysis of HER and ORR. It is reported that the Co-N\textsubscript{4} derived from ZIF-67 has been widely recognized as active sites for ORR in both acidic and alkaline solutions\textsuperscript{55-56}. Figure 5 presents the differences of Gibbs free energy of Co-N\textsubscript{4}-C, Pt NPs and the combination of Co-N\textsubscript{4}-C and Pt NPs during the HER process in alkaline. It is observed that the energy barrier for the OH-H bond cleavage on Co-N\textsubscript{4}-C and Pt NPs are 2.26 eV and 1.07 eV, respectively, while the water dissociation energy barrier on the combination of Co-N\textsubscript{4}-C and Pt NPs decrease to only 0.73 eV. The decrease in the dissociation energy barrier suggests the combination of Co-N\textsubscript{4}-C and Pt NPs can significantly accelerate the dissociation of water to H\textsubscript{ads}, resulting in the fast kinetics of HER because the dissociation of water is the rate-limiting step of the HER in alkaline media. An ideal HER catalyst is expected to have a moderate hydrogen binding energy (HBE) in the step of the conversion of H\textsuperscript{*} to H\textsubscript{2}, balancing the H\textsuperscript{*} adsorption and subsequent H\textsubscript{2} desorption on the
surface of catalysts. The HBE on Co-N₄-C and Pt NPs are 1.10 eV and 0.49 eV, respectively, much stronger than the optimal value (0 eV), resulting in the suppressing H* desorption and subsequently hindering H₂ generation. In contrast, the combination of Co-N₄-C and Pt NPs shows a more moderate HBE value of 0.23 eV, suggesting the combination of Co-N₄-C and Pt NPs is more efficient catalyst for the production of H₂ compared with the Co-N₄-C and Pt NPs. Based on the above discussion, synergistic effects between the Co-N₄-C and Pt NPs can improve the HER activity in alkaline media through accelerating fast kinetics of HER by lowering the energy barrier for water dissociation and adjusting the HBE. In acid media, compared with the Co-N₄-C and Pt NPs, the combination of CoN₄ and Pt NPs displays the lowest HBE of 0.23 eV, approaching the optimal value (0 eV), which facilitates the H* adsorption and H₂ desorption on the surface of the electrocatalysts and thereby leads to high HER activity. This finding indicates the synergistic effects between the Co-N₄-C and Pt NPs also improve the HER activity in acid media.

Figure 5. Calculated free energy diagram of the HER on different active sites. (a) In alkaline (b) in acid medium. Here TS represents a transition state of H₂O activation.

DFT calculations were also carried out to confirm the synergistic catalysis of Pt-based NPs and Co-N₄ derived from ZIF-67 during ORR Process. In our calculation, the Pt-based NPs are idealized as Pt (111). The detail DFT calculations process for ORR is provide in supporting information.
As shown in Figure 6a, the kinetic barrier for OOH* formation on a Co-N4 site is only <0.1 eV, which is close to that of Pt site. However, on the only Co-N4-C active sites, it will form of O* and water and produce H2O2 after the formation of *OOH. When Pt (111) sites in the vicinity to Co-N4-C active sites, the H2O2 generated on Co-N4 active sites can spillover to adjacent Pt (111) sites to produce H2O (Figure 6b). This finding suggests that the synergistic effects between the Co-N4-C and Pt NPs can help catalysis of O2 on the Co-N4-C active sites to H2O instead of H2O2.

![Free-energy diagram of the ORR pathways](image)

**Figure 6.** (a) Free-energy diagram of the ORR pathways. The blue line represents the Co-N4-C active site and pink line represents the Pt (111) active site. (b) The Calculated structural model of the ORR pathways for Co-N4-C and the combination of Co-N4-C and Pt NPs.

- **Conclusions**
In summary, we propose a facile approach to synthesize highly active and stable electrocatalysts by encapsulating Pt NPs with precisely control of ultrathin carbon layers derived from the ultrathin 2D MOF precursor. The ultrathin 2D carbon layers not only provides a suitable protecting layers for stabilizing Pt NPs and but also introducing highly dispersed active sites. Our Pt catalysts encapsulated in the ultrathin 2D carbon layers exhibited show higher stability with enhanced activity towards ORR and HER in comparison with commercial Pt/C catalyst. The enhanced performance of our encapsulated Pt catalysts are attributed to the synergetic effect of Pt-based NPs and ultrathin 2D carbon layers derived from ZIF-67 with enriched in active sites of Co-Nx. First-principles simulations reveal that the synergistic catalysis of Pt-based NPs and Co-N4 derived from ZIF-67 improve the activity for ORR and HER. The general synthetic approach presented in this work provides a promising candidate for the development of high performance of metal catalysts.

■ EXPERIMENTAL SECTION

**Synthesis of Pt/GO:** Graphene oxide was obtained by a modified Hummers method according to the previous study.41 Pt/GO was synthesized as follows: 290mg hexachloroplatinum (IV) acid (H2PtCl6·6H2O) was added to ethylene glycol and stirred for 0.5 h. The pH of the solution was adjust to about 11 by addition of NaOH. Subsequently, the solution was heated to 200 °C in an oil bath and kept at this temperature for 3 hours. After cooling down to room temperature, the EG solution containing 400 mg graphene oxide was added to the black mixture to deposit Pt nanoparticles on GO. The HCl was added to accelerate the deposition of Pt nanoparticles on GO. After stirring for 1 hours, Pt/GO was obtained by centrifugation and washing several times with deionized water and then freeze-dried.

**Synthesis of X-ZIF-67-Pt/GO:** 800 mg Co (NO3)2·6H2O was dissolved in 400 ml methanol solution containing 200 mg Pt/GO and stirred for 1 hour. The Pt/GO adsorbed Co ions was
obtained by centrifugation and washed with ethanol. Then the Pt/GO adsorbed Co ions was dissolved again in 400 ml methanol containing 2-methylimidazole (800 mg). After stirring for 1h, the sample was achieved by centrifugation and washed with ethanol. The obtained sample was recorded as 1ZIF-67-Pt/GO. Sample 3ZIF-67-Pt/GO and 5ZIF-67-Pt/GO were obtained after repeating the above procedure 3 times and 5 times, respectively. The samples of X-ZIF-8-Pt/GO was prepared based on the above procedure with Zn(NO$_3$)$_2$·6H$_2$O and 2-methylimidazole.

**Synthesis of Pt/RGO:** The 200 mg sample Pt/GO in a quartz boat was heating-treated at 600 °C for 3 h under N$_2$ atmosphere, and the sample Pt/RGO was obtained. The Pt loading for Pt/RGO is 22.3 wt% by ICP.

**Synthesis of X-ZIF-67-Pt/RGO:** All the samples X-ZIF-67-Pt/GO were placed in a quartz boat, and heated to 600 °C in N$_2$ atmosphere for 3 hours. The carbonized material was acid washed by 1 M HCl for 2 hours to remove residual Co species. Finally, the material were dried at 60°C under vacuum to achieve the X-ZIF-67-Pt/RGO. The Pt loading for 1ZIF-67-Pt/RGO, 3ZIF-67-Pt/RGO and 5ZIF-67-Pt/RGO is 20.3 wt%, 17.2 wt% and 15.7 wt%, by ICP, respectively.

**Synthesis of PtCo/RGO:** Appropriate amount of H$_2$PtCl$_6$·6H$_2$O, CoCl$_2$·6H$_2$O and GO were added to 150 ml ethylene glycol and ultra-sonicated for 1h. The pH of the mixture was adjusted to about 10 using NaOH. The mixture was heating-treated at 160 °C for 3 h. PtCo/RGO was obtained by centrifugation and washing several times with deionized water and then freeze-dried. Then sample was treating at 600°C for 3h at 10%H$_2$/90%N$_2$ to obtain PtCo/RGO.

**Synthesis of 3ZIF-67/RGO:** 800 mg Co (NO$_3$)$_2$·6H$_2$O was added to 400 ml methanol solution containing 200 mg GO and stirred for 1 hour. The GO adsorbed Co ions was obtained by centrifugation and washed with ethanol. Then the GO adsorbed Co ions was dissolved again in 400 ml methanol containing 2-methylimidazole (800 mg). After stirring for 1h, the sample was...
obtained by centrifugation and washed with ethanol. Sample 3ZIF-67/GO was obtained after repeating the above procedure 3 times. Sample 3ZIF-67/GO were heated at 600 °C for 3 hours in N₂ atmosphere. The carbonized material was then acid washed by 1 M HCl for 2 hours to remove residual Co species. Finally, the material were dried under vacuum to obtain the 3-ZIF-67/RGO.

**Materials characterization:** The thickness of the samples were characterized by Atomic Force Microscope (AFM, Agilent 5500). Scanning electron microscopy (SEM) was performed on a SUPRA 55. Transmission electron microscopy (TEM) images and Wide-angle X-ray diffraction (XRD, D-MAX 2200 VPC) patterns. The particle size distribution were calculated by measuring more than 200 Pt nanoparticles using Nano Measurer. X-ray photoelectron spectroscopy (XPS) characterization was performed by a K-Alpha. Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (iCAP7000, Thermo Fisher Scientific) was used to determine the Pt loading.

**Electrochemical Characterization:** All electrochemical measurements were tested in a three-compartment cell at room temperature on an Autolab electrochemical workstation. We used Platinum wire, Ag/AgCl electrode a rotating disk electrode (RDE) as the counter, reference and working electrodes, respectively. The potentials in this work were converted to RHE according to \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{pH}. \) The uniform catalyst ink was prepared by mixed 4 mg catalyst powder and 2 ml solution containing 990μL deionized water, 990 μL isopropanol and 20 μL Nafion ionomer solution. The ink was then coated on RDE (0.196 cm²) and the mass loading of Pt was 20 μg·cm⁻². Before measurements, a steady CV of the working electrode was firstly obtained by cycling at 0.05-1.2 V at 50 mV·s⁻¹ in a N₂-saturated 0.5 M H₂SO₄ solution. An oxygen reduction reaction (ORR) linear sweep voltammetry (LSV, 10 mV·s⁻¹) was performed in O₂-saturated 0.5 M H₂SO₄. The hydrogen evolution reaction (HER) test use a three-electrode cell in alkaline solution (1M KOH, pH=14) and acidic solution (0.5 M H₂SO₄, pH=0). A graphite rod instead of Pt wire
was used as a counter electrode. For HER tests, the final Pt loading of all samples was 10 μg·cm⁻². Note all the HER LSV tests were 100% iR compensated.

**ASSOCIATED CONTENT**

**Supporting Information**

Computational method & mechanistic discussion, AFM and additional TEM images, additional XPS spectra, additional polarization curves, additional EDS mapping and Calculated structural model. The following files are available free of charge.

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**Notes**

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References


