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Non-precious alloy encapsulated in nitrogen-doped graphene layers derived from MOFs as an active and durable hydrogen evolution reaction catalyst

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Non-precious metal based catalysts are emerging as the most promising alternatives to Pt-based ones for hydrogen evolution reaction (HER) due to its low cost and rich reserves. However, its low efficiency and stability due to inherent corrosion and oxidation in acid media are the main barriers blocking sustainable hydrogen production. Metal-organic frameworks, with both designable metal ion centers and organic ligands, are promising precursors for the one-step synthesis of metal/alloy@carbon composites for HER. Herein, we synthesized FeCo alloy nanoparticles encapsulated in highly nitrogen-doped (8.2 atom%) graphene layers by direct annealing of MOFs nanoparticles in N\textsubscript{2}. The catalyst shows low onset overpotential (88mV) and an overpotential of only 262 mV at 10 mAcm\textsuperscript{-2}. Besides, it exhibits an excellent long-term durability performance even after 10000\textsuperscript{th} cycles due to the protection of graphene layers. Our density function theory calculations reveal that the nitrogen dopants can provide adsorption sites for H* and the proper increasing of nitrogen will decrease $\Delta G_{\text{H}*}$ for HER. Besides, the unique structure of metal and graphene composites derived from MOFs can also decrease the $\Delta G_{\text{H}*}$ thereby promoting catalytic activity.
Hydrogen, as a clean and renewable energy, has attracted growing attention owing to the declining availability of fossil fuels.\textsuperscript{1-4} The electrocatalytic hydrogen evolution reaction (HER) is a chemical reaction of water splitting to produce H\textsubscript{2} at the cathodic side of the electrolyzer and holds extensive interest due to its high energy conversion efficiency.\textsuperscript{5} For HER, Pt-based or Pd-based catalysts have been regarded as the most efficient electrocatalyst.\textsuperscript{6} However, the high cost and scarcity of them hinder their commercialization.\textsuperscript{7,8} In the past decade, large efforts have been devoted to explore low cost and efficient non-previous alternatives for Pt-based catalysts, mainly including metal carbides (Mo\textsubscript{2}C, W\textsubscript{2}C),\textsuperscript{9,10} metal nitrides (Co\textsubscript{0.6}Mo\textsubscript{1.4}N\textsubscript{2}, MoN),\textsuperscript{11,12} metal sulphides (MoS\textsubscript{2}, CoS\textsubscript{2})\textsuperscript{13,14} and metal phosphides (Ni\textsubscript{2}P, FeP).\textsuperscript{15,16} Very recently, 3d transition metals and their alloys encapsulated in carbon based materials are emerging as promising candidates for HER catalysts.\textsuperscript{17-19} Bao et al synthesized a FeCo alloy encapsulated in nitrogen doped carbon nanotubes.\textsuperscript{17} Kari Laasonen et al obtained single-shell carbon-encapsulated iron nanoparticles with excellent catalytic activity.\textsuperscript{18} The strategy of combining non-precious metal core with carbon shell can simultaneously promote the activity and stability of the material through the synergism and protection from carbon cage.\textsuperscript{19} However, nearly all previous works are using complex and expensive CVD methods or multi-step synthesis process, hindering the large scale commercialization. What’s more, both experimental and theoretical results indicating the nitrogen doping can significantly improve the property of carbon-based material for HER. Nevertheless, the nitrogen content of materials mentioned above is confined by CVD or post treatment method. Metal-organic frameworks (MOFs) exhibit a strong potential for use as templates and reactive precursors for fabricating nanostructured materials via thermolysis.\textsuperscript{20-22} Our group has ever developed a process to prepare highly nitrogen doped carbon and its composite materials using MOF compounds as precursors.\textsuperscript{23-25} Through changing metal ion centers (such as Fe, Co, Ni, Cu) and designing organic ligands with different dopants (N, P, S atoms), various alloys covered with doped graphene layers might be obtained from carefully designed MOFs precursors, which could be promising HER catalysts. Prussian blue analogues (PBA), with CN\textsuperscript{-} groups as linkers,
transition metal (Fe, Co, Mn and so on) as metallic nodes which is rich in nitrogen, provides an ideal precursor for the fabricating of highly nitrogen doped carbon with non-precious metals. Inspired by this, we adopted a facile synthesis of FeCo alloy encapsulated in highly nitrogen doped graphene layers by one-step annealing of Fe$_3$(Co(CN)$_6$)$_2$ nanoparticles. The material exhibits excellent long-term stability for HER due to the protection of graphene shell. The nitrogen content in the material is also changeable under different annealing temperatures. According to density function theory, nitrogen doping can not only provide adsorption sites for H* but also decrease $\Delta G_{H*}$ for HER. Previous study also proves that the properties of materials are sensitive to the structure and morphology of materials. Therefore, the unique structures as well as the high nitrogen contents derived from MOFs contribute to the excellent and durable HER performance.

Fe$_3$(Co(CN)$_6$)$_2$ spheres were synthesized according to our previous research and were used as MOF precursor for further annealing treatment. The SEM image of the MOF precursor particles was illustrated in Figure S3, the diameter of the particles was about 1 µm. The MOF precursor was directly carbonized under a nitrogen flow under different temperatures (600°C, 700°C, 800°C) without adding any other carbon sources. Fe$_3$(Co(CN)$_6$)$_2$, with CN$^-$ groups as linkers, transition metal (Fe, Co) as metallic nodes, which is rich in nitrogen, carbon as well as metal atoms, provides an ideal precursor for the preparation of composite materials of highly nitrogen doped carbon with non-precious metals (Scheme 1a). During the annealing process under N$_2$, Fe and Co atoms from the precursor will form FeCo alloy nanoparticles under high temperatures, meanwhile some CN$^-$ group linkers will serve as both carbon and nitrogen sources for the formation of nitrogen doped graphene layers outside the alloy particles (In situ formation process as illustrated in Scheme 1d). The in situ formed graphene layers will avoid the agglomeration of FeCo nanoparticles to provide more active sites for HER (Scheme 1c). Moreover, the nitrogen doped graphene shells will also protect the alloy core from corrosion so as to enhance the durability of the catalyst. Besides, such a unique structure with alloy core and nitrogen-doped graphene shell can realize the synergism between metal and carbon matrix which is beneficial.
to the HER process. The resulting product inherits the morphology of sphere and is like a model of “plum-pudding”: FeCo alloys were encapsulated in nitrogen doped graphene layers like plums which were uniformly distributed in sphere “pudding” (Scheme 1b). Scheme 1 illustrates the synthetic route and model of a FeCo alloy particle encapsulated in nitrogen doped graphene layers.

**Scheme 1** The synthetic route and model of the FeCo alloys encapsulated in nitrogen doped graphene layers. (a) Fe$_3$[Co(CN)$_6$]$_2$ sphere, the picture inside is the crystalline structure of Fe$_3$[Co(CN)$_6$]$_2$ containing a three-dimensional network of Fe–C≡N–Co, (b) An aggregate of FeCo alloys encapsulated in graphene layers, (c) Enlarged model of an FeCo alloy particle encapsulated in nitrogen doped graphene layers as a catalyst for hydrogen production, the HER process follows a Volmer–Heyrovsky mechanism. (d) In situ formation of FeCo alloys in Fe$_3$[Co(CN)$_6$]$_2$ sphere and FeCo alloys-catalyzed formation of nitrogen doped graphene layers using C and N sources derived from the decomposition of Fe$_3$[Co(CN)$_6$]$_2$.

The samples obtained under different temperatures were designated as S-600, S-700, S-800 respectively. All the samples show a sphere-like morphology with a diameter of approximately 600 nm according to the field emission scanning electron microscopy (FESEM) results (Fig. 1a, 1b and Fig S2 a,b.). The transmission electron microscopy
(TEM) image of S-600 (Fig. 1c) illustrates the sphere product is composed of small encapsulated alloy particles. High resolution transmission electron microscopy (HRTEM) (Fig. 1d and 1e), especially enlarged image (Fig. 1f) further revealed small alloy particles were coated with graphene layers (about 5 layers). The enlarged HRTEM image of S-600, S-700, and S-800 (Figure S4, S5, S6) illustrated that the graphene layers of alloy particles are in the range of 3 to 8 layers. As shown in Fig. 1g-i, the images of elemental mapping by energy filtered TEM (EFTEM) reveal that the Fe and Co element are uniformly distributed in the particle, further confirming the alloy structure of FeCo.

Figure 1 (a-c) the field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) image of S-600, (d-e) high resolution transmission electron microscopy (HRTEM) of the S-600, (f) enlarged image of 1e where interplanar spacing of alloy as well as graphene shell were measured in the image, (g-i) STEM image of the single FeCo nanocrystal and the images of elemental
Nitrogen sorption experiments were measured to obtain information on the specific surface area and pore size of the samples. The adsorption/desorption isotherms were shown in Figure S11. The Brunauer–Emmett–Teller (BET) specific surface area of the S-600 particles was calculated to be 66.2 m$^2$/g. The pores exhibited a strong and narrow distribution centered at 2.5 nm, which should be formed during annealing process and the replication of high porosity of MOF precursor. Some of the small pores may connect with each other, leading to some larger pores, reflecting a weak and wide size distribution in Figure S11. These results were in good agreement with the morphology of S-600 in Figure 1, the spherical samples were composed of many small aggregated FeCo particles.

The XRD patterns of the encapsulated alloy particles (S-600, S-700, S-800) were shown in Fig. 2a. Similar diffraction features of them were observed, the characteristic peaks at 44.8° and 65.3° correspond to the (110) and (200) planes of the FeCo alloy (JCPDS 49-1567), respectively. No other impurity peaks were observed in the XRD patterns. Besides, a broad and weak peak of C (002) was also detected, confirming the existence of carbon.

**Figure 2** (a) The XRD patterns of S-600, S-700, S-800; (b) Raman spectra of S-600.

Figure 2b and Supplementary Fig S9 showed the Raman spectra of the obtained graphene coated alloy particles. The high I$_D$/I$_G$ band intensity ratio of samples
indicates the generation of large amounts of defects, which suggests that large N atoms are doped in graphene layers in our samples. In addition, a broad and weak second-order band was observed at approximately 2,700 cm\(^{-1}\) for all the samples and the shape of the D and 2D bands are characteristic features of few-layered graphene.\(^{28,29}\)

The X-ray photoelectron spectroscopy (XPS) spectra of samples were illustrated in Fig S8 and the detailed content of samples are listed in Table S1. It should be noted that the Fe and Co content in the samples surface is very low, further indicating the alloy particles are completely coated with nitrogen doped graphene shells. From the table, we can see that with the increasing of annealing temperatures, the nitrogen content of the sample is decreasing. The nitrogen content of S-600 is the highest among the three samples with nitrogen content of 8.2 atom%. The N1s spectrum of S-600 can be deconvoluted into four individual peaks that are assigned to pyridinic N (398.7 eV), pyrrolic N (399.9, 400.7 eV), and quaternary N (401.6 eV), respectively (As showed in Fig 3).\(^{23,30-32}\) It should be noted that pyrrolic N has two binding energies here which might be ascribed to the energy shift induced by the interaction of some pyrrolic N with metal atoms.\(^{33}\) The percentage of pyridinic, graphitic and pyrolic nitrogen was 56.0%, 27.3% and 16.7%, respectively.

**Figure 3** The XPS result of N1s spectrum for S-600.
The catalytic activity of the alloy samples for the HER was evaluated using a standard three-electrode electrochemical system in 0.5M H$_2$SO$_4$ with a flow of N$_2$ during the HER experiment. The electrocatalytic activity of commercial Pt catalyst (40 wt% Pt/C) was measured as a reference. In addition, pure graphene and pure metal Co encapsulated in nitrogen doped graphene layers (Co/graphene) were also prepared and evaluated for comparison. The detailed measurement and synthesizing methods can be seen in the supporting information. All the measured catalysts were deposited on a glassy carbon electrode with 3 mm diameter (loading 0.285 mg cm$^{-2}$).

The polarization curves of samples were illustrated in Fig 4a, the pure graphene exhibited a poor HER activity. The HER catalytic activity of Co/graphene was far better than pure graphene, however, inferior to the samples of alloy. The performance of S-800, S-700, S-600 were improved sequentially with the increased nitrogen contents in graphene layers, besides the S-600 exhibited the best catalytic activity with a small onset overpotential of about 88mV and overpotential of only 262 mV at 10 mAcm$^{-2}$ versus reversible hydrogen electrode (RHE). Tafel plots of the FeCo alloys obtained under different temperatures were shown in Fig 4b, which were usually used to reveal the inherent reaction mechanism of the HER. The Tafel plots of S-800, S-700, S-600 were 80, 74, 74 mV/dec respectively indicating that the HER process is likely to occur by a Volmer-Heyrovsky mechanism.$^{34,35}$ The electrochemically active surface area (ECSA) of samples were estimated using a simple cyclic voltammetry method (detailed information is in supporting information). The result suggested that with the increasing density of catalytically active sites of samples, the catalytic performance of them would also be improved.

The durability of S-600 was also assessed by measuring of polarization curves after particular cyclic voltammetric (CV) sweeps as illustrated in Fig 4c. The polarization curve of S-600 after 10 000$^{th}$ cycles retained an almost similar performance to the initial test and the TEM image of the sample after 10000$^{th}$ cycles still maintained the original morphology (Fig S2c). We also measured the i-t curve of S-600 at overpotential of 300 mV vs RHE for more than 10 h. As illustrated in Fig S14, the
current density of S-600 only showed a slight decrease in the first three hours and remained almost unchanged during following testing hours, besides the current density after 11 h was also larger than 10 mA, further confirming the stability of our material. To our knowledge, the long-term durability demonstrated in our measurements is rarely seen or reported for non precious-metal HER catalysts in acidic media. We compared our material with some other non-precious/carbon based catalysts in Table 1.\cite{17,19,36,37} From the table, it was found that our material showed a promising catalytic activity especially cycling stability. The stable performance of S-600 was ascribed to the unique structure derived from MOFs. The graphene shell of the alloy would protect the core of alloy from corrosion during cycling, besides the alloy distributed uniformly in the sphere might also be beneficial to the HER.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading amount (mg/ cm²)</th>
<th>Overpotential at 10 mA cm⁻² (mV)</th>
<th>Overpotential at 10 mA cm⁻² (mV) after certain cycles</th>
<th>Synthesis method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-600</td>
<td>0.285</td>
<td>262</td>
<td>276, 2000th 286, 10000th</td>
<td>Direct annealing of MOFs</td>
<td>This work</td>
</tr>
<tr>
<td>FeCo@NCNTs-NH</td>
<td>0.32</td>
<td>276</td>
<td>About 350, 10000th</td>
<td>CVD method</td>
<td>Energy Environ. Sci., 2014, 7, 1919-1923</td>
</tr>
<tr>
<td>CoNi@NC</td>
<td>0.32</td>
<td>224</td>
<td>About 260, 1000th</td>
<td>Multistep bottom-up method</td>
<td>Angew. Chem. Int. Ed. 2015, 54, 1-6</td>
</tr>
</tbody>
</table>
Table 1 Non-precious/carbon based catalysts for HER in acid media. Some of the information was not specified in the literature and was estimated according to data graphs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Overpotential (V vs RHE)</th>
<th>Cycle</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Co@G</td>
<td>0.285</td>
<td>About 280, 100th</td>
<td>Multistep hydrothermal method</td>
<td>ACS Appl. Mater. Interfaces 2015, 7, 8083–8087</td>
</tr>
<tr>
<td>Ni–Sn@C</td>
<td>0.1</td>
<td>About 350</td>
<td>Multistep chemically etching method</td>
<td>Acs Appl Mater Inter, 2015, 7, 9098-9102</td>
</tr>
</tbody>
</table>

Figure 4 (a) The polarization curves of samples versus RHE, (b) the Tafel plots of S-800, S-700, S-600, (c) the polarization curves of S-600 after 1st, 2000th, 5000th, 10000th cycles, (d) calculated $\Delta G_{H^*}$ diagram of some models, the words in the bracket means the H* adsorbed on whether graphene or Co side.

To better understand the origin of the high activity of the samples especially the role
of the nitrogen doping, density functional theory (DFT) calculations were carried out using the Vienna Ab Initio Simulation Package (VASP), with supplied Projector Augmented Wave (PAW) potentials for core electrons. The detail of calculation was in supporting information. $\Delta G_{\text{H*}}$ is one of the key descriptors in theoretical prediction of the activity for HER on solid electrodes. A good catalyst of the HER should have a moderate free energy ($\Delta G_{\text{H*}}$ close to 0) for H adsorption to compromise the reaction barriers of the adsorption and desorption steps.\textsuperscript{38}

We calculated the $\Delta G_{\text{H*}}$ of pure graphene and graphene doped with three different types of nitrogen (graphitic, pyridinic and pyrrolic nitrogen as illustrated in Fig 5) according to the XPS results. As shown in Fig 4d, the pristine graphene exhibited a large $\Delta G_{\text{H*}}$ of 2.503 eV indicating a negligible adsorption ability of H*. However, all of the three nitrogen doped graphene models showed improved $\Delta G_{\text{H*}}$ especially of graphitic and pyrrolic nitrogen. Interestingly, the H* was far away from pristine graphene sheet while showed a stable adsorption with the C atom next to the nitrogen after doping as shown in Fig 5a, b. Using bader population analysis, we compared the electronegativity of three different nitrogen atoms in their doping models. The calculated results showed that pyridinic, graphitic and pyrrolic nitrogen could accept different charge from neighbour carbon atoms (the calculated charge transfers were 1.20, 1.12 and 0.87 |e|, respectively). Previous work based on molecular orbital theory proved that different electronegativity of doping atoms would lead to variation of valence orbital which had linear trend in relation with $\Delta G_{\text{H*}}$.\textsuperscript{39} Therefore, the different electronegativity of three nitrogen would tailor electronic structure of neighbour carbon atoms at different levels, resulting in different $\Delta G_{\text{H*}}$. Moreover, the different adsorption sites and configurations might also induce the change of $\Delta G_{\text{H*}}$.\textsuperscript{40} As a result, better performance of pyrrolic N than the other two nitrogen atoms might be ascribed to the proper electronegativity and configuration after doping. We also calculated the model with more nitrogen atoms doping. In order to reduce calculation cost, only graphitic N doping was considered. The graphene with two graphitic nitrogen showed a $\Delta G_{\text{H*}}$ of 0.042eV, very close to zero. This result indicated that proper increasing of nitrogen content will improve the catalytic performance of graphene. Even though we
could not control the nitrogen doping on specific position as we calculated so far, it was a fascinating method to exactly control the electronic structure and chemical property of the material and worth future studying. The charge-density difference of H* adsorbed on graphitic nitrogen doped graphene was illustrated in Fig 6. It showed that the electrons transferred from C atom (next to nitrogen) to H*, subsequently increasing the charge density of the C-H bond. These results confirmed that the nitrogen doping would provide H* adsorption sites for graphene and proper increasing of nitrogen content would further enhance the adsorption ability, which was also consistent with the catalytic performance of samples under different annealing temperatures. The thickness of graphene shell and size distribution of alloy particles would also influence the performance of catalyst according to previous researches.  

From the enlarged HRTEM images (Figure S4, S5 and S6), the layers of graphene shells are not uniform in all samples. However, all of our three samples exhibited similar range of graphene layers (3-8 layers), as a result, the influence of nonuniform layers in the samples might be counteracted. We also calculated the average size of FeCo alloy in our samples by statistical analysis of the alloy particles near the edge (the particles inside sphere is hard to distinguish due to overlap). Most of the particles were within the range of 10-20 nm and the average sizes of alloy in S-600, S-700 and S-800 were 14.8, 16.6, 17.4 nm, respectively. The average crystallite sizes of the samples were also calculated by Scherrer's equation from X-ray diffraction patterns and the results were about 16, 19 and 20 nm, respectively, which were almost consistent with our statistical results. These results indicated that the size of alloy would increase with the increase of annealing temperature. With the increasing of annealing temperature, the crystal grains would form larger clusters with gathering of much more nearby grains, and crystal grain growth will proceed within the cluster, resulting in the increased size of alloy particles. However, the difference of average sizes was very small and most of the particles were within the range of 10-20 nm. The slight difference of particle size and graphene layers might influence the electrochemical performance to some extent, however, the influence was small in our samples compared with nitrogen doping based on our calculation results and above
We also calculated the $\Delta G_{H^*}$ of pure metal models (Co$_4$ and Co$_2$Fe$_2$), the model was showed in Fig S1). Both of the two models showed relative negative $\Delta G_{H^*}$ (-1.206 and -0.284 eV) which would be disadvantageous to the desorption step. While the $\Delta G_{H^*}$ of alloy (Co$_2$Fe$_2$) was closer to zero than pure metal Co$_4$, it indicated the better performance of alloy than pure metal which was also consistent with our experiment results. Previous studies showed that the formation of heteroatom bonds and alteration of the bond length would lead to ligand and strain effects which would result in shift of the metal’s d-band center and an optimized $\Delta G_{H^*}$. When Fe atoms were doped to Co$_4$ cluster, the Co-Co bond length was changed and the new bond length of Fe-Co (2.18 Å) and Fe-Fe (2.56 Å) after doping were also different from Co-Co (2.22 Å) before doping, which might induce the effects mentioned above, resulting an optimized $\Delta G_{H^*}$.

Figure 5 Optimized structure of H* adsorbed on (a) pure graphene (b-d) graphitic,
pyrrolic and pyridinic nitrogen doped graphene. The model was illustrated both from
top view and side view.

![Figure 6](image)

**Figure 6** Charge-density difference of H* adsorbed on graphitic nitrogen doped
graphene.(a) graphene doped with one nitrogen atom (b) graphene doped with two
nitrogen atoms. The isosurface value of the color region is 0.09 e Å^{-3}. The yellow and
cyan regions refer to increased and decreased charge distributions, respectively.

The synergistic effect between metal and graphene had been studied in previous
works. Herein, we also investigated the synergistic effect with a Co₄ cluster above the
graphene sheet. Even though the metal cluster was smaller than that in the samples, it
should not undermine the reliability of DFT for investigation of the effect by this
simple model. The calculation result was illustrated in Figure S12. The metals were
bonded with both carbon and nitrogen atoms, as illustrated in Figure S12a, the Co-N
bond length was 2.04 Å and Co-C bond length was between 2.04 and 2.12 Å. From
charge-density difference calculation (Figure S12b), we noticed that the electrons
were transferred from Co atoms to C atoms in the graphene, which also proved the
bonding interactions between metal and graphene sheet. The transferred electrons
from metal to C atoms were consistent with previous work and regarded as a benefit
to improve the HER activity.¹⁷,¹⁹ It should be noted that for the combination of metal
and graphene model, the H* might be adsorbed on both metal side and graphene side.

For the models without nitrogen doping (Co₄/gra), the situation of H* adsorbed on
Co$_4$ side exhibited a moderate $\Delta G_{\text{H}*}$ which almost approximate zero (0.001 eV), however, the H* adsorbed on graphene side possessed a very positive $\Delta G_{\text{H}*}$ of 2.535 eV. Meanwhile, the models with nitrogen doping (Co$_4$/N-gra) showed relative moderate $\Delta G_{\text{H}*}$ (as illustrated in Fig 4d) close to zero on the both adsorption sides (-0.263 and 0.427 eV) indicating the enhanced catalytic performance after nitrogen doping. On the metal side, Co$_4$/gra (0.001 eV) dose have a superior $\Delta G_{\text{H}*}$ than Co$_4$/N-gra (-0.263 eV) which might be ascribed to different electronic structure of Co atoms after nitrogen doping. However, it should be noted that the difference of $\Delta G_{\text{H}*}$ of metal side was very small compared with graphene side: Co$_4$/gra (2.535 eV) versus Co$_4$/N-gra (0.427 eV). Besides, the calculations on the interaction between metal clusters and graphene showed the charge-transfer occur from metal to graphene sheet, indicating the enhancement of property was mainly manifested on the graphene side (Figure S12). Even though we calculated both situations of adsorption in theory, the main adsorption sites should be on the graphene side in practice, since the metal alloy were nearly totally encapsulated by graphene layers in our material. Therefore, the models with nitrogen doping still showed better performance in our calculations after overall consideration.
Figure 7(a-b) Models of Co4/graphene with the adsorption of H* on the graphene side and metal side, (c-d) models of Co4/N-graphene with the adsorption of H* on the graphene side and metal side. The model was illustrated both from top view and side view.

In summary, we adopted a facile method to synthesize the FeCo alloys encapsulated in nitrogen doped graphene layers. By controlling of annealing temperature, samples doping with different nitrogen contents were obtained. Electrochemical measurements showed that S-600 with the highest nitrogen doping content displays the best HER activity. Compared with other metal/carbon based HER catalysts, our material exhibited promising catalytic performance especially long term stability after 10000th cycles. DFT calculations indicated that the superior HER performance originated from the decreasing of $\Delta G_{H^*}$ of nitrogen dopants as well as the metal-graphene composite structure. Proper amount of nitrogen dopant can increase the H* adsorption sites which further enhances the HER activity. What’s more, the unique structure of
graphene shell and alloy core of the material ensures a very stable performance even after 10000th cycles. Other metal or alloy materials coated with carbon shell might be also obtained by this process via simply changing metal ion centers or ligands of MOF precursor. These findings pave the way towards the development of high-performance, inexpensive and long cycling HER electrocatalysts in acidic media.

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Reference


