Strain-Driven Bimetallic-Interface Orbital Hybridization for Hydrogen Evolution Reaction

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ABSTRACT: Enforcing the bimetallic-interface orbital hybridization in single-atom catalysts (SACs) plays a critical role in determining their catalytic activity. However, the electronic state coupling among interacting sites can be affected by surficial strain, but the relative physical mechanism still needs to be understood. Herein, we propose a series of bimetallic-hybridized SACs with structural strain to disclose their interfacial charge transfer and orbital interaction, in which asymmetric superexchange interaction between adjacent Fe and Ni sites can enforce their electronic state coupling by a structural deformation. As a result, the spin-resolved electronic structure, d-band center, and Gibbs free energy can be changed by external strain, leading to a higher reactive activity. Our findings provide a new insight into understanding the contribution of surface strain to enhancing their catalytic activity.

INTRODUCTION

On the journey to exploit clean energy to overcome the environmental degradation, water splitting into hydrogen has been considered as an ideal energy due to its high energy capacity.1−3 It is of great interest to utilize particular catalysts with low cost and high activity to acquire hydrogen from electrocatalytic water splitting, especially in the light of industrial application. Based on this consideration, developing economical and abundant catalysts, such as transition meal dichalcogenides, nitrides, sulﬁdes, and phosphides, has been proposed to replace noble metal Pt-based catalysts.4−10 However, the overall performance is still unsatisfactory, and the lack of stable, efﬁcient, and inexpensive catalysts remains a principal problem. Generally speaking, an ideal catalyst should simultaneously possess enough active sites (large superﬁcial area), good reactive activity (suitable Gibbs free energy), and fast carrier transfer (good metallic feature).11,12 These fundamental factors strongly depend on the catalyst’s electronic structure, which can be easily regulated by structural strain, especially for two-dimensional materials.

In this respect, single-atom catalysts (SACs) display an obvious advantage in energy-related electrocatalysis,13−15 in which the metal active sites are randomly distributed and their stronger interactions between adjacent metal sites with a smaller intersite distance can alter the electronic structure. From the viewpoint of classical catalytic theory,16 the reactive activity of the active site can be evaluated by the Gibbs free energy, which is strongly related with the electronic occupation at metal t2g and eg orbitals. The exchange interaction can make some valence electrons transfer to one metal site from another adjacent site, leading to an electronic reconfiguration. The exchange interaction strength is proportional to the intersite distance. When SACs are fabricated experimentally, the distribution of the metal site has been customized but partial residual strain can inevitably affect their interaction to some extent,9,10 especially for a smaller intersite distance. More importantly, the implantation of structural strain makes the catalytic behavior governed by individual and interacting sites become more complex. However, the relative physical mechanism and catalytic application in hydrogen evolution reaction (HER) are yet to be understood.

To avoid complex experiments and better understand the strain contribution, the comprehensive density functional theory (DFT) predication can be considered as a feasible strategy. Herein, the Fe−N4, Ni−N4, and Fe−N4@Ni−N4 moieties with different intersite distances are purposely bonded onto graphene to discuss the contribution of strain response onto their electronic structure transformation, orbital interaction, and charge transfer. The calculations demonstrate that the Fe−N4@Ni−N4 catalysts with asymmetric superexchange interaction can lead to a higher HER performance than pristine Fe−N4 and Ni−N4. More interestingly, the strain response becomes more sensitive when the intersite distance between the Ni site and Fe site is decreased to 2.294 Å, in which partial valence electrons of the Fe site can transfer to the neighboring...
Ni site, leading to a spin-related bonding interaction for adsorbed hydrogen and reactive sites. As a result, the Gibbs free energy and carrier transfer capacity can be obviously enhanced.

**COMPUTING METHOD**

The theoretical calculations were performed by DFT using Vienna Ab initio Simulation Package codes. In this process, the generalized gradient approximation and Perdew–Burke–Ernzerhof pseudopotentials were adopted to expand the Kohn–Sham wave functions.\(^\text{17,18}\) Additionally, the energy cutoff is 460 eV and Monkhorst-Pack \(k\)-points are \(10 \times 10 \times 1\), which have been tested to be well converged. All the forces on the free ions were set to 0.01 eV/Å, and a vacuum space of 18 Å was adopted to construct the surfaces. Based on Dudarev’s method,\(^\text{19}\) the effective Hubbard contribution was considered to describe the strong electron–electron interaction for transition metals, such as Fe (\(U = 2.0\) eV) and Ni (\(U = 1.0\) eV). The relative spin polarizations have been included in our calculations, in which the spin-resolved electronic structures were calculated by combining the DFT with the Heyd-Scuseria-Ernzerhof (HSE06) functional method.\(^\text{20}\) More importantly, the van der Waals interactions were also

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**Figure 1.** (a–d) Atomic configuration and charge density difference for one Fe–N\(_4\) site and Ni–N\(_4\) located in graphene with different intersite distances.

**Figure 2.** Spin density (a) and spin-resolved DOS (b) for one Fe–N\(_4\) site and Ni–N\(_4\) located in graphene with an intersite distance of \(D = 5.640\) Å. The spin density for hydrogen adsorbed onto Fe (c) and Ni (d) sites.
considered by the dispersion-corrected DFT method (optB88-vdW).

■ RESULTS AND DISCUSSION

To understand the atomic configuration, the Ni—N$_4$ site and Fe—N$_4$ site with different charge densities are bonded onto graphene with different distances and are compared in Figure 1a–d. Note that the yellow regions correspond to the charge decrease and the green ones represent the charge increase. As a general feature, the anchor of each metal site can lead to an electronic redistribution, in which the valence electrons of the metal site can be acquired by the neighboring N atoms to form Fe—N bonds or Ni bonds. More importantly, the redistribution of the electronic wave function will generate a coupling effect with decreasing intersite distance. For example, when the Fe—Ni distance is decreased as $D = 2.294$ Å, as shown in Figure 1a, the coupling electronic states make the Fe site reserve more valence electrons, which can be assessed quantitatively by the Bader charge as Fe = 7.0795 e and Ni = 9.1464 e. For a larger Fe—Ni distance such as $D = 5.640$ Å, the coupling effect between bimetallic hybridization can be weak, which makes the Bader charge of Fe decrease to 6.9267 e but that of Ni increase to 9.1506 e. This can be explained by the fact that the overlapping of electronic redistribution between two metal sites is obviously decreased. With increasing the distance for the Fe—Ni bond in Figure 1c, the charge of the Fe atom is decreased to 6.9042 e and the charge of Ni is increased to 9.1592 e. When the distance of the Fe—Ni bond is further increased to 11.688 Å, as displayed in Figure 1d, the charge of the Fe site can be decreased ulteriorly to 6.8946 e. This comparison discloses the fact that the orbital hybridization and exchange interaction between neighboring metal sites are strongly dependent on their distance. To better understand the electronic configuration, the distributions of valence electrons at e$_g$ and t$_{2g}$ orbitals are compared in Figure S1 in the Supporting Information. For the Fe—N$_4$ site, the t$_{2g}$ orbitals are completely occupied and the e$_g$ orbitals with an asymmetric filling displays a higher spin state. In contrast, no unpaired spin electrons can be observed at Ni-e$_g$ orbitals, in which one empty e$_g$ orbital can be used to accept the charge transfer from the Fe site. More interestingly, the difference at spin-resolved electronic occupation can lead to an obviously different spin polarization. In addition, the atomic configurations for two single Ni—N$_4$ sites and Fe—N$_4$ sites located at graphene with different distances are displayed in Figures S2 and S3 in the Supporting Information. When the distance between two neighboring metal sites is decreased, their electronic exchange interaction will be enforced, leading to more observable changes in catalytic activity. It is interesting to note that the metal atoms acting as active sites are mainly fixed by the neighboring N and C atoms, which plays a critical role in determining structural stability.

To confirm the spin-related reactive activity, the spin charge densities between spin-up and spin-down are calculated and shown in Figure 2a. It can be observed that the spin charge densities are all distributed at Fe sites and no relative spin polarization appears at the Ni site. Therefore, a magnetic moment of 1.986 $\mu_B$ appears at the Fe site, but that of the Ni site is 0.00 $\mu_B$. To confirm this point, the spin-resolved project density of states (DOS) for this bimetallic hybridized atom configuration is displayed in Figure 2b. We can see that the DOSs of Ni-3d orbitals are symmetrically distributed for the

Figure 3. (a) Bader charge of the Fe site at the Fe@Fe hybridized SAC as a function of external strain. (b) Bader charge of the Ni site at the Ni@Ni hybridized SAC as a function of external strain. The Bader charge of Fe (c) and Ni (d) sites for the Fe@Ni hybridized SAC as a function of external strain.
spin-up and spin-down ones, displaying no spin polarization. For the Fe element, the DOSs with spin-down appear at the nearby Fermi level but those of the spin-up ones are far away from the Fermi level, which leads to obvious spin splitting. This difference in DOS distribution can be attributed to the different electronic fillings at $e_g$ and $t_{2g}$ orbitals. When the Fe site is used as the active site to react with adsorbed hydrogen, as shown in Figure 2c, the magnetic moment of the Fe site sharply decreases to $0.963 \mu_B$; meanwhile, the spin density becomes delocalized. Some spin density appears at the region nearby the Ni site, leading to a $\sim 0.021 \mu_B$ magnetic moment. If the active site is changed as the Ni site, as shown in Figure 2d, the adsorbed hydrogen can lead to a different spin polarization. In this process, the magnetic moment of the Fe site decreases to $1.820 \mu_B$ but that of the Ni site can lead to a $0.163 \mu_B$ spin polarization. It is concluded that the spin-related charge transfer and orbital interaction at the neighboring Fe−Ni site play a critical role in determining catalytic activity in HER.

To disclose the contribution of external strain, the Bader charges of metal sites as a function of external strain for the pristine Fe−Fe hybridized SAC are calculated and shown in Figure 3a. In this work, the compressive strain and tensile strain are mainly defined with reference to the lattice constant of the equilibrium state. When the lattice constant is smaller than the lattice constant at the equilibrium state, the structural deformation is defined as compressive strain and is tensile strain vice versa. It can be observed that the values of the Fe site with a smaller distance possess higher charges, and they are decreased with structural deformation, especially for compressive strain. In addition, the strain response for type1 is more sensitive than that for type2, type3, and type4, which indicates that the contribution of external strain can be enforced for stronger electronic state coupling. When two metal sites are replaced by Ni atoms, as shown in Figure 3b, the Bader charges of Ni atoms are obviously different from that of Fe sites but they are also linearly reduced with external strain. It is important to note that the change gradient for type1 is obviously larger than that of type2, type3, and type4. When the metal site is composed of one Fe and one Ni atom, the difference in electronic occupation makes their interaction become different from pristine Fe or Ni SACs. This is because the radial distribution function for Fe and Ni-3d orbitals is obviously different, which could lead to an asymmetric superexchange interaction. As shown in Figure 3a, the charges of the Fe site in bimetallic structures are generally smaller than that of the pristine Fe structure. More interestingly, the charge of the Fe site for type1 can cross with the type2-type4 with increasing external strain, demonstrating a higher strain response. However, the changes in the Ni site for this bimetallic SAC are not sensitive, which is similar to that of the Fe site, as shown in Figure 3d. These changes in Bader charge disclose the facts that the electronic occupation can be obviously affected by the structural deformation and a smaller interdistance between metal sites can lead to a stronger electronic state coupling.

To display the influence of strain onto the electronic state, the spin-resolved DOSs for the bimetallic SACs with different external strains are calculated. Compared with the pristine Fe SAC, the spin splitting between spin-down and spin-up in the Fe@Ni hybridized SAC can be changed due to charge transfer and redistribution, as shown in Figure 4a. More importantly, some electronic states are compelled by 3% compressive strain to cross the Fermi level, displaying a metallic feature. Instead, the 3% tensile strain in Figure 4b makes DOSs become far

Figure 4. Spin-resolved DOS for Fe-3d orbitals at different SACs with a 3% compressive strain (a) and tensile strain (b). The spin-resolved DOS for Ni-3d orbitals at different SACs with a 3% compressive strain (c) and tensile strain (d).
away from the Fermi level, demonstrating a semiconducting behavior. The good metallic feature for the Fe@Ni hybridized SAC with compressive strain provides a feasible strategy to accelerate carrier transfer. As a comparison, the spin-resolved DOSs for the Ni site in SACs with 3% compressive strain and tensile strain are provided in Figure 4c,d, respectively. Different from that of Fe elements, the electronic occupations for the Ni-3d orbital are all far away from the Fermi level, which are not sensitive to the structural deformation. In addition, they are symmetrically distributed, and no obvious spin polarization can be observed. This can be easily understood by the fact that the symmetric electronic occupation at the eg orbital can form a more stable bonding interaction, which cannot be easily affected by external strain. This behavior is obviously different from that of the Fe site which displays an obvious electronic reconstruction under a compressive strain.

To assess the changes in catalytic activity, the Gibbs free energies of hydrogen adsorbed onto Fe sites in the pristine Fe@Fe SAC as functions of external strain are calculated in Figure 5a. It is universally known that the optimal $\Delta G_H$ is zero, in which the adsorbed hydrogen can bond with the active site neither too strongly nor too weakly. The positive Gibbs free energy means that the hydrogen cannot be adsorbed onto the active site because of a weaker bonding interaction between hydrogen and metal sites. It can be found that the $\Delta G_H$ values can be sharply decreased by compressive strain, especially for type1. In addition, the $\Delta G_H$ values of Fe sites are obviously smaller than that of the Ni site at the Ni@Ni hybridized SAC, which can be reflected by the calculations in Figure 5b. This is because the Fe site with unpaired valence electrons at eg orbitals can easily accept the electron of hydrogen, leading to a stronger bonding interaction. However, this particular electronic occupation cannot occur at the Ni site, which makes the $\Delta G_H$ of the Ni site become larger. More interestingly, the $\Delta G_H$ of the Fe site and Ni site can be effectively decreased when they form a bimetallic hybridized structure, as shown in Figure 5c,d. After careful comparison, we can conclude that the exchange interaction between Fe and Ni sites with a smaller distance (such as type1) is more sensitive to external strain. The 3% compressive strain makes the $\Delta G_H$ of the Fe site at type1 tend to zero, leading to an expected catalytic activity. In contrast, the $\Delta G_H$ change in the Ni site prefers tensile strain more. These comparisons disclose that bimetallic hybridization between Fe and Ni sites with a smaller distance can lead to a higher catalytic activity by applying a compressive strain. Interestingly, the Bader charges for Fe and Ni sites as a function of external strain are slightly different from the changes in Gibbs free energy. This is because the bonding or antibonding interactions between reactants and active sites are strongly depended on their electronic occupation at half-filled 3d orbitals. The empty 3d orbitals can be used to accept the electrons of reactants, leading to a higher bonding interaction, which is beneficial for reactant adsorption. For reactant dissociation, half-filled 3d orbitals will transfer to the reactants from the catalysts, corresponding to an antibonding interaction. In fact, the HER process should be mutually determined by the cooperation effect between adsorption and dissociation, which can be directly reflected by the Gibbs free energy. The Bader charge can demonstrate the charge transfer and electronic configuration induced by this strain-responsive bimetallic hybridization, but that cannot give the real electronic occupation at half-filled 3d orbitals. Therefore, a different trend for Gibbs

Figure 5. Gibbs free energy for the Fe site at Fe@Fe (a) and Fe@Ni (c) hybridized SACs as a function of external strain. The Gibbs free energy for the Ni site at Ni@Ni (b) and Fe@Ni (d) hybridized SACs as a function of external strain.
free energy and Bader charge as functions of external strain occurs.

To disclose the change in HER activity, the d-band centers for different SACs as functions of external strain are calculated and compared in Figure 6a–d. Generally, a larger value of the d-band center corresponds to a higher catalytic activity because the valence electrons at eg orbitals can generate a bonding interaction with reactants. As shown in Figure 3, the charge of the metal site can be affected by the external strain, which can affect the position of the d-band center. The calculations disclose that the d-band center of the Fe site is obviously larger than that of the Ni site and they also can be changed by external strain, as the comparison shown in Figure 6a,b. In addition, the asymmetric exchange interaction between Fe and Ni sites can further increase their values, as shown in Figure 6c,d, which can be used to explain why a good ΔG_H occurs at the Fe site of the Fe@Ni SAC. In addition, the contribution of strain onto d-band center shift also can be reflected.

To disclose the reaction process, the crystal Hamilton population (COHP) between the reactive site and adsorbed hydrogen for the Fe@Ni SAC with different strains is calculated and compared, as shown in Figure 7a. For 3% compressive strain, the COHP intensity at the Fermi level is obviously stronger than that of 3% tensile strain, which discloses a stronger antibonding interaction between the Fe site and adsorbed hydrogen. In this case, the reactants can be dissociated from the Fe site more easily, which gives rise to a smaller ΔG_H. When the compressive strain is applied onto this

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Figure 6. d-Band center for the Fe site at Fe@Fe (a) and Fe@Ni (c) hybridized SACs as a function of external strain. The d-band center for the Ni site at Ni@Ni (b) and Fe@Ni (d) hybridized SACs as a function of external strain.

Figure 7. (a) COHP for Fe–H bonds of the Fe@Ni hybridized SAC with different strains. (b) Charge intensity difference for hydrogen adsorbed onto the Fe site.
system, the valence electrons can occupy the Fermi level to display a metallic behavior, benefiting to hybridize with adsorbed hydrogen. In contrast, the tensile strain could lead to an opposite effect. To intuitively confirm this behavior, the charge density difference for hydrogen adsorbed onto the Fe site is provided in Figure 7b, where the yellow regions correspond to charge decrease; meanwhile, the blue regions represent the charge increase. In this process, the adsorbed hydrogen can provide partial value electrons to occupy the Fe-eg orbital, in which the charge of Fe is decreased to 7.0275 e from 7.0407 e. More importantly, the electronic reconfiguration at Fe-eg orbital makes its magnetic moment decrease from 7.0407 e. More importantly, the electronic reconstructions induced by active sites and exchange interaction between active sites induced by external strain can directly affect the bonding interaction with reactants.

### CONCLUSIONS

In conclusion, the exchange interaction and orbital hybridization between bimetallic SACs can be effectively regulated by structural strain. With the decrease in intersite distance, the electronic state coupling between two metal sites can be enforced, which is more sensitive to external strain. The spin-related electronic structure discloses the fact that the compressive strain can make the Fe site acquire more valence electrons to occupy the Fermi level, displaying a metallic behavior. Therefore, the carrier transfer ability and catalytic activity can be improved simultaneously. However, this influence cannot be observed by applying tensile strain. This work provides a new insight into regulating the electronic structure and reactive activity of SACs by combining with residual strain.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01772.

Electronic occupation at Fe and Ni sites and atomic configurations for Fe–N$_4$ and Ni–N$_4$ sites located in graphene with different intersite distances (PDF)

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**Notes**

The authors declare no competing financial interest.

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