



# Article Computational Design of Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> Clusters for Multifunctional Electrocatalysts

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**Abstract:** High-efficiency and low-cost multifunctional electrocatalysts for hydrogen evolution reaction (HERs), oxygen evolution reaction (OERs) and oxygen reduction reaction (ORRs) are important for the practical applications of regenerative fuel cells. The activity trends of core–shell  $Ni_6@M_{32}$  and  $Ni_6@Pt1M31$  (M = Pt, Pd, Cu, Ag, Au) were investigated using the density functional theory (DFT). Rate constant calculations indicated that  $Ni_6@Pt_1Ag_{31}$  was an efficient HER catalyst. The Volmer–Tafel process was the kinetically favorable reaction pathway for  $Ni_6@Pt_1M_{31}$ . The Volmer–Heyrovsky reaction mechanism was preferred for  $Ni_6@M_{32}$ . The Pt active site reduced the energy barrier and changed the reaction mechanism. The ORR and OER overpotentials of  $Ni_6@Pt_1Ag_{31}$  were calculated to be 0.12 and 0.33 V, indicating that  $Ni_6@Pt_1Ag_{31}$  could be a promising multifunctional electrocatalyst.  $Ni_6@Pt_1M_{31}$  core–shell clusters present abundant active sites with a moderate adsorption strength for \*H, \*O, \*OH and \*OOH. The present study shows that embedding a single Pt atom onto a Ni@M core–shell cluster is a rational strategy for designing an effective multifunctional electrocatalyst.

Keywords: DFT; single-atom catalyst; core-shell; HER; ORR; OER

# 1. Introduction

Reversible fuel cells or unitized regenerative fuel cells (URFCs) combine the functions of fuel cells and electrolyzers, which attract increasing attention because of their high levels of efficiency and environmentally friendly merits [1]. The key challenge is to develop highly active and stable multifunctional electrocatalysts for hydrogen and oxygen electrode reactions [2,3]. The cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER) have sluggish kinetics due to large overpotentials. Pt/C and noble metal oxides of RuO<sub>2</sub> and IrO<sub>2</sub> demonstrated advanced activity with reduced overpotentials in ORR/HER/OER processes [4–6]. However, the wider applications of noble-metal materials have been limited by their high price and scarcity [7,8]. Thus, efforts are mainly devoted to the design of efficient and cheap catalysts whose catalytic performances are comparable to noble metals in accelerating the ORR, OER and HER [9–13].

Recently, electrocatalysts with core–shell structures were prepared to be applicable for catalyzing the ORR/OER/HER efficiently [14,15]. The electronic structure of a core–shell cluster can be regulated through the electronic interaction between the core and shell [16]. Many core–shell nanoclusters have been explored theoretically and experimentally for the ORR process [17–19]. A novel Pt core–shell catalyst for the ORR was reported with an impressive improvement, producing 3.7 times greater results relative to a Pt/C material [20]. Chen and colleagues reported that Ni-Pd alloys with Pd-enriched surfaces exhibited significantly enhanced ORR activities and improved CH<sub>3</sub>OH tolerances compared to Pd/C catalysts [21]. Lin et al. reported the synthesis of snap-bean-like, multi-dimensional core/shell Ni/NiCoP nano-heterojunctions (NHs), presenting improved stability and activity for both hydrogen evolution reactions (HERs) and oxygen evolution reactions (OERs) [22]. Ma et al. demonstrated a core–shell-structured non-noble-metal,



Citation: Jia, J.; Tian, D. Computational Design of Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> Clusters for Multifunctional Electrocatalysts. *Molecules* **2023**, *28*, 7563. https://doi.org/10.3390/ molecules282227563

Academic Editor: Minghao Yu

Received: 13 June 2023 Revised: 29 June 2023 Accepted: 10 July 2023 Published: 13 November 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Ni@In, loaded on silicon nanowire arrays (SiNWs) for the efficient reduction of CO<sub>2</sub> to formate [23]. Park's group synthesized a Ni-based core–shell material (Ni@Ni-NC) which displayed excellent electrocatalytic OER performance with over- and onset potentials of 371 mV and 1.51 V, respectively, which are superior to those of commercial IrO<sub>2</sub> [24], and Yu's group found that Ni@Pd core–shell nanoparticles exhibited robust ORR activity and stability in both acidic and alkaline electrolytes, comparable to commercially available Pt/C catalysts [25]. In addition, Lang's group prepared binary core–shell Ni@Pt NPs [26] with good ORR performance and durability. A Ni<sub>19</sub>@Pt<sub>70</sub> cluster exhibited better catalytic activity and stability for the ORR than Pt<sub>79</sub> [27].

With nearly 100% atom utilization, a unique local coordination environment and electronic configuration, noble-metal single-atom catalysts (SACs) exhibit unique properties [28–32]. Li's group predicted that the Pt<sub>1</sub>/PMA (phosphomolybdic acid cluster) catalyst is a promising multifunctional electrocatalyst for use in water splitting ( $\eta^{\text{HER}} = 0.02 \text{ V}$  and  $\eta^{\text{OER}} = 0.49 \text{ V}$ ) and a metal–air battery ( $\eta^{\text{ORR}} = 0.79 \text{ V}$ ) [33]. Zhao et al. reported a single-atom Ru catalyst for the OER with the overpotential of 118 mV [34]. Zhang et al. proposed a single-atom Au electrocatalyst supported by NiFe-LDH with high activity for the OER [35].

A multifunctional electrocatalyst should have abundant active sites which remarkably facilitate the adsorption/desorption of \*H, \*O, \*OH and \*OOH intermediates and products or two reactions simultaneously. The adsorption and desorption energies of the reaction species should be moderate, according to the Sabatier's principle [36].

We systematically investigated the stability and multifunctional catalytic behavior of Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag, Au) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au) for the ORR, OER and HER using DFT calculations. The OER overpotential of Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> ( $\eta^{OER} = 0.33$  V) is lower than RuO<sub>2</sub> ( $\eta^{OER} = 0.37$  V) [34] and IrO<sub>2</sub> ( $\eta^{OER} = 0.56$  V) [37]. Rate constant calculations indicated that Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> is an efficient HER catalyst. The Volmer– Tafel process was a kinetically favorable reaction pathway for Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>, while the Volmer–Heyrovsky process was the major pathway for Ni<sub>6</sub>@M<sub>32</sub>. The present study shows that embedding a single Pt atom onto core–shell Ni@PtM cluster is a rational strategy for designing a multifunctional electrocatalyst.

# 2. Results and Discussion

#### 2.1. Structure and Stability Analysis

A core–shell Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag, Au) cluster (Figure 1) was used as a catalyst model to understand the activity trends of the HER, OER and ORR. The average bond lengths were calculated and are shown in Table S2. The average bond lengths of the Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag, Au) clusters were shorter than those of pure M<sub>32</sub> clusters arising from a lattice mismatch between the core and shell atoms. The average bond length of the shell decreases in the following order: Ni<sub>6</sub>@Au<sub>32</sub>  $\approx$  Ni<sub>6</sub>@Ag<sub>32</sub> > Ni<sub>6</sub>@Pd<sub>32</sub> > Ni<sub>6</sub>@Pt<sub>32</sub> > Ni<sub>6</sub>@Cu<sub>32</sub>.

The formation energies of the Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> structures were calculated according to Equation (S1) and are presented in Table 1. The negative values indicate that it is thermodynamically favorable for the formation of Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> from Ni<sub>6</sub>@M<sub>32</sub> and a Pt atom. The thermodynamic trend is Ni<sub>6</sub>@Pt<sub>1</sub>Pd<sub>31</sub> (-0.56 eV) > Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> (-0.51 eV) > Ni<sub>6</sub>@Pt<sub>1</sub>Cu<sub>31</sub> (-0.08 eV) > Ni<sub>6</sub>@Pt<sub>1</sub>Au<sub>31</sub> (0.33 eV).

The average binding energy was calculated according to Equation (S2) and is presented in Figure 2a. The average binding energy decreases in the following order:  $Ni_6@Pt_{32}$ (4.53 eV) >  $Ni_6@Pd_{32}$  (4.36 eV),  $Ni_6@Pt_1Pd_{31}$  (4.40 eV) >  $Ni_6@Pt_1Au_{31}$  (3.02 eV),  $Ni_6@Au_{32}$ (2.96 eV) >  $Ni_6@Pt_1Ag_{31}$  (2.63 eV),  $Ni_6@Ag_{32}$  (2.53 eV) >  $Ni_6@Pt_1Cu_{31}$  (0.42 eV),  $Ni_6@Cu_{32}$ (0.25 eV).  $Ni_6@Pt_{32}$  has the highest binding energy (4.53 eV) and is the most stable catalyst.

A Bader charge analysis was carried out to investigate the electronic properties of the Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>. The electronegativities (Pauling scale) of Ni, Pt, Pd, Au, Ag and Cu are 1.91, 2.28, 2.20, 2.54, 1.93 and 1.90, respectively. As presented in Figure 2b, the charge transfer amount changes in the following order: Ni<sub>6</sub>@Pt<sub>32</sub> > Ni<sub>6</sub>@Pd<sub>32</sub>, and Ni<sub>6</sub>@Au<sub>32</sub> > Ni<sub>6</sub>@Ag<sub>32</sub> > Ni<sub>6</sub>@Cu<sub>32</sub>. The charge transfer amount increases with the increased difference in the electronegativity between the core and shell elements. It

is closely related to the average binding energy, as shown in Figure S1. The average binding energy increases with an increased amount of charge transferred between the core and shell.



**Figure 1.** The structures of  $Pt_{38}$ , Pt (111), core–shell  $Ni_6@M_{32}$  (M = Pt, Pd, Cu, Ag, Au) and  $Ni_6@Pt_1M_{31}$  (M = Pd, Cu, Ag, Au) clusters. T, b, f and hollow represent the top, bridge, face and hollow site, respectively.

Table 1. The fe	ormation	energies	of the	$Ni_6@Pt_1M_{31}$	structures.
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<b>Reaction Coordination</b>	$E_{\rm f}/{\rm eV}$
$Ni_6@Pd_{32} + Pt_1 \rightarrow Ni_6@Pt_1Pd_{31} + Pd_1$	-0.56
$Ni_6@Cu_{32} + Pt_1 \rightarrow Ni_6@Pt_1Cu_{31} + Cu_1$	-0.08
$Ni_6@Ag_{32} + Pt_1 \rightarrow Ni_6@Pt_1Ag_{31} + Ag_1$	-0.51
$Ni_6@Au_{32} + Pt_1 \rightarrow Ni_6@Pt_1Au_{31} + Au_1$	0.33



**Figure 2.** (a) Average binding energies for core–shell clusters. (b) Bader charge transfer amounts between the cores and shells of clusters.

The density of the states projected onto the d states of the Ni<sub>6</sub>@M<sub>32</sub> clusters and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au) clusters is shown in the Figure S2. The introduction of a Pt atom narrows the distribution of the d states. Its influence is smaller on the Ni<sub>6</sub>@Pd<sub>32</sub> cluster than on the other three clusters. The Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> cluster shows the most significant change in its PDOS compared to the Ni<sub>6</sub>@Ag<sub>32</sub> cluster, with the population of high-energy

states decreasing and the population of low-energy states increasing. This feature may present active sites with a moderate adsorption strength for \*H, \*O, \*OH and \*OOH.

#### 2.2. Hydrogen Evolution Reaction (HER) Catalytic Activity

Mechanistically, the HER involves three possible principal steps in acidic media which occur via either the Volmer–Heyrovsky or Volmer–Tafel process as presented in Text S1. The Volmer reaction refers to the initial adsorption of protons from the acid solution to form adsorbed H and is usually considered to be fast. The Heyrovsky reaction refers to the reaction of a proton in the water layer with an adsorbed hydrogen to form  $H_2$ . Two adsorbed H atoms react to form  $H_2$ , which is Tafel reaction process.

#### 2.2.1. The Hydrogen-Adsorption Gibbs Free Energies of Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>

To assess the Volmer performance of the Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag, Au) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au), we calculated the differential hydrogen-adsorption Gibbs free energy (d $-\Delta G_{H^*}$ ) and average-hydrogen-adsorption Gibbs free energy (a $-\Delta G_{H^*}$ ) values (Equations (S3)–(S5) in Text S1) as functions of the hydrogen coverage ( $\theta_{H^*}$ ). Here,  $\theta_{H^*}$  was defined as n/6, where n is the number of adsorbed H atoms. The exchange current density value *i*<sub>0</sub> was calculated as a function of d $-\Delta G_{H^*}$  according to the Equations (S6) and (S7) in Text S1. The d $-\Delta G_{H^*}$  and a $-\Delta G_{H^*}$  values of Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au) from  $\theta_{H^*} = 1/6$  to 6/6 are presented in Figure 3a,b,d,e,g,h,j,k. A volcano relation formed between d $-\Delta G_{H^*}$  and the exchange current density. The volcano plot of *i*<sub>0</sub> as a function of d $-\Delta G^*_{H}$  is presented in Figure 3c,f,i,l. For comparison, data regarding Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag, Au), including the d $-\Delta G_{H^*}$  a $-\Delta G_{H^*}$  and *i*<sub>0</sub> values, are presented in Figure S3.

For Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Pt), the high hydrogen coverage value ( $\theta_{H^*} = 6/6$ ) corresponds to the optimal  $d - \Delta G_{H^*}$  and  $i_0$  values. For example, for Ni<sub>6</sub>@Pt<sub>1</sub>Pd<sub>31</sub>, the  $d - \Delta G_{H^*}$  values were calculated to be -0.28, -0.23, -0.25, -0.12, -0.33 and 0.10 eV at a H coverage ranging from 1/6 to 6/6, and the volcano plot indicates that the high  $\theta_{H^*} = 6/6$  corresponds to the low  $d - \Delta G_{H^*}$  and high  $i_0$  values. Compared with the Ni<sub>6</sub>@Pd<sub>32</sub> cluster (Figure S3), the  $d - \Delta G_{H^*}$  and  $a - \Delta G_{H^*}$  values of Ni<sub>6</sub>@Pt<sub>1</sub>Pd<sub>31</sub> are closer to zero, demonstrating the benefit of the introduction of single-site Pt. For Ni<sub>6</sub>@M<sub>32</sub> (M = Cu, Ag, Au) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Ag, Au), the low hydrogen coverage ( $\theta_{H^*} = 1/6$ ) value corresponds to the optimal  $d - \Delta G_{H^*}$  and high  $i_0$  values.

The repulsion interaction between neighboring negatively charged, adsorbed \*H atoms possibly improves the desorption. At low H coverage, Ni<sub>6</sub>@M<sub>32</sub> (M = Cu, Ag, Au) present d- $\Delta G_{H^*}$  and  $i_0$  values which are comparable to Ni<sub>6</sub>@Pt<sub>32</sub>. The optimal  $|d-\Delta G_{H^*}|$ ,  $|a-\Delta G_{H^*}|$  and  $i_0$  values and the Bader charges of the hydrogen atoms in the Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> systems are presented in Table S3. These results show the complex influence of the hydrogen coverage on the interaction between the adsorbate and the adsorption site. An analysis of the projected density of states (PDOS, Figure S4) shows that high coverage can broaden the distribution of the d-DOS of the adsorption sites for the Ni<sub>6</sub>@Pd<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>Pd<sub>31</sub> clusters. This weakens the adsorption strength of the adsorbates at the adsorption site.

## 2.2.2. The Energy Barriers of the Tafel and Heyrovsky Processes

From the point of the adsorption free energy, at a low H coverage, Ni<sub>6</sub>@M<sub>32</sub> (M = Cu, Ag, Au) present Volmer activity comparable to Pt-based Ni<sub>6</sub>@Pt<sub>32</sub>. We further investigated the kinetic properties of all candidates. Considering the water environment, the energy barriers of the Tafel and Heyrovsky processes were calculated for Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>, with a  $d-\Delta G_{*H}$  value close to zero. Figure 4 displays the structures of the adsorption state, transition state and product species and the energy barriers. The energy barriers of the Tafel process for Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au) are 0.33, 0.21, 0.10 and 0.55 eV, respectively. We employed the H<sub>3</sub>O species to consider the H<sub>3</sub>O<sup>+</sup> + e<sup>-</sup> approximately for the simulation of the Heyrovsky step. The energy barriers of the Heyrovsky process were calculated to be, respectively, 0.89, 0.88, 0.45 and 0.77 eV. For Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Au), the

Heyrovsky process needs to overcome a relatively higher energy barrier to form H<sub>2</sub> by H<sub>3</sub>O reacting with an adsorbed H\*. The Volmer–Tafel reaction mechanism is main pathway for Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au) by combining two adsorbed hydrogens to form H<sub>2</sub>. The energy barriers of the Tafel process for Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag) are 0.55, 0.66, 0.78 and 1.06 eV, respectively, as presented in Figure S6. The energy barriers of the Heyrovsky process for Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag) are 0.43, 0.54, 0.14 and 0.70 eV, respectively. The Volmer–Heyrovsky reaction pathway is favorable for Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag).



**Figure 3.** The differential Gibbs free energy profiles  $(d - \Delta G_{H^*})$  over the Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au) clusters (**a**,**d**,**g**,**j**); the average Gibbs free energy profiles  $(a - \Delta G_{H^*})$  (**b**,**e**,**h**,**k**); the volcano plot of  $i_0$  as a function of  $d - \Delta G_{H^*}$  at the best H coverage (**c**,**f**,**i**,**l**); the highlight in blue denotes the free energy window of  $\pm 0.25$  eV.



**Figure 4.** The potential energy profiles of the HER via the Tafel process and the Heyrovsky process at the optimal H coverage. 6H-Ni<sub>6</sub>@Pt<sub>1</sub>Pd<sub>31</sub> (**a**,**b**), 4H-Ni<sub>6</sub>@Pt<sub>1</sub>Cu<sub>31</sub> (**c**,**d**), 2H-Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> (**e**,**f**) and 2H-Ni<sub>6</sub>@Pt<sub>1</sub>Au<sub>31</sub> (**g**,**h**). White, red, blue, coppery, grey and golden ball represent H, O, Ni, Cu, Ag and Au, respectively.

The rate constants (k/s) of the Tafel and Heyrovsky processes in the HER were calculated according to Equation (S8), based on the Eyring transition state theory with Wigner correction [38], as presented in Table 2. By comparing the rate constants, the

Volmer–Heyrovsky reaction mechanism was determined to be favorable for  $Ni_6@M_{32}$ , and the Volmer–Tafel process was determined to be a kinetically advantageous reaction pathway for  $Ni_6@Pt_1M_{31}$ . The Pt active site decreases the energy barrier and modulates the reaction mechanism.

**Table 2.** Rate constants (k/s) and energy barriers of the Tafel and Heyrovsky processes in the HER on Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au).

System	$\Delta G_{\mathrm{Tafel}}^{ eq}/\mathrm{eV}$	Tafel (k/s)	$\Delta G_{ m Heyrovsky}^{ eq}/ m eV$	Heyrovsky (k/s)
6H-Ni <sub>6</sub> @Pt <sub>32</sub>	0.55	$4.35  imes 10^3$	0.43	$3.92  imes 10^5$
6H-Ni <sub>6</sub> @Pd <sub>32</sub>	0.66	54.4	0.54	$4.78 imes10^3$
2H-Ni <sub>6</sub> @Cu <sub>32</sub>	0.78	0.72	0.14	$3.17 imes10^{10}$
3H-Ni <sub>6</sub> @Ag <sub>32</sub>	1.06	$1.84 imes10^{-5}$	0.70	9.84
6H-Ni <sub>6</sub> @Pt <sub>1</sub> Pd <sub>31</sub>	0.33	$1.76  imes 10^7$	0.89	$6.17 imes10^3$
4H-Ni <sub>6</sub> @Pt <sub>1</sub> Cu <sub>31</sub>	0.21	$1.84  imes 10^9$	0.88	$9.25  imes 10^{-3}$
2H-Ni <sub>6</sub> @Pt <sub>1</sub> Ag <sub>31</sub>	0.10	$1.83 imes10^{11}$	0.45	$1.69 imes10^5$
2H-Ni <sub>6</sub> @Pt <sub>1</sub> Au <sub>31</sub>	0.55	$3.27 \times 10^3$	0.77	0.64

Platinum metal catalysts have been known as the most efficient catalysts for the HER due to their optimum Gibbs free energy for atomic hydrogen adsorption ( $\Delta G_{H^*}$ ). Ni<sub>6</sub>@Cu<sub>32</sub> has comparable HER activity to Ni<sub>6</sub>@Pt<sub>32</sub>, and at  $\theta_{H^*} = 2/6$ , Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> is the most efficient catalyst of Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>. These results indicate the H coverage is an important factor in the kinetic activity of the HER.

#### 2.3. The Oxygen Reduction Reaction (ORR)/Oxygen Evolution Reaction (OER): Catalytic Activity

The activity of the ORR and OER under acidic conditions were investigated for Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>. It was given that the oxygen reduction reaction pathway occurs via an associative mechanism, with four protonation reaction steps. The adsorption free energies of the oxygenated intermediates were calculated as presented in Table S4 via the computational hydrogen electrode (CHE) model, using hydrogen and water as references, according to Equations (S18)–(S21). The free energy diagram of the four-electron reaction is presented in Figure 5. The OER/ORR overpotential was obtained by Equations (S22) and (S23). As shown in Figure 4, the ORR's potential-limiting step is the proton-coupled electron transfer step  $*OH \rightarrow H_2O$  for Pt<sub>38</sub>, Pt (111), Ni<sub>6</sub>@Pt<sub>1</sub>Cu<sub>31</sub> and Ni<sub>6</sub>@M<sub>32</sub> (M = Pd, Cu, Ag, Au). The potential-limiting step of the ORR's elementary reactions for  $Ni_6@Pt_1M_{31}$ (M = Pd, Au) is  $O_2 + H^+ + e^- \rightarrow *OOH$ . For  $Ni_6@Pt_{32}$  and  $Ni_6@Pt_1Ag_{31}$ ,  $*O \rightarrow *OH$ is the potential-limiting step. The ORR overpotentials are presented in Table S5. The overpotential ( $\eta^{\text{ORR}}$ ) values of the Pt (111) and Pt<sub>38</sub> clusters were calculated to be 0.73 and 0.81 V. For  $Ni_6@Pt_1M_{31}$  (M = Pd, Cu, Ag, Au), the overpotentials were calculated to be 0.77, 0.83, 0.12 and 1.06 V, respectively.  $Ni_6@Pt_1Ag_{31}$  showed the best activity, with  $\eta^{\text{ORR}}$  = 0.12 V. In the OER process, the potential-limiting step is the \*O  $\rightarrow$  \*OOH step for  $Pt_{38}$ , Pt (111), Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Au). For Ni<sub>6</sub>@Cu<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub>, the OER's potential-limiting step is the \*OOH  $\rightarrow$  O<sub>2</sub> process. The second deprotonation process (\*OH  $\rightarrow$  \*O) is the OER's potential-limiting step for Ni<sub>6</sub>@M<sub>32</sub> (M = Ag, Au). The OER overpotentials for Pt<sub>38</sub> and Pt (111) are 1.34 and 0.74 V. The OER overpotentials for the Ni<sub>6</sub>@ $M_{32}$  (M = Pt, Pd, Cu, Ag, and Au) clusters are 1.17, 0.81, 0.92, 0.93 and 1.08 V, respectively. The calculated OER overpotentials for  $Ni_6@Pt_1M_{31}$  (M = Pd, Cu, Ag, Au) are respective 1.36, 1.61, 0.33 and 0.61 V. The OER overpotential for a Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub>  $(\eta^{\text{OER}} = 0.33 \text{ V})$  single-atom catalyst is lower than those of RuO<sub>2</sub> ( $\eta^{\text{OER}} = 0.37 \text{ V}$ ) [37] and  $IrO_2 (\eta^{OER} = 0.56V)$  [37].



**Figure 5.** The Gibbs energy diagrams for the ORR and OER for (a)  $Pt_{38}$ , Pt (111), (b)  $Ni_6@M_{32}$  (M = Pt, Pd) and  $Ni_6@Pt_1Pd_{31}$ , (c)  $Ni_6@M_{32}$  (M = Cu, Ag, Au), (d)  $Ni_6@Pt_1Pd_{31}$  (M = Cu, Ag, Au) at U = 0 V (RHE).

The adsorption strength of the three intermediates, \*OOH, \*O and \*OH, was analyzed to explore the activity trend of the Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>32</sub> (M = Pd, Cu, Ag, Au). As shown in Figure 6a,b, there is a linear relationship between the adsorption free energy values of \*OOH and \*OH. The inverted volcano curve was obtained by plotting the adsorption free energy of \*OH and the corresponding ORR overpotential, as presented in Figure 6c. On the left leg, the rate-limiting step is the \*OH  $\rightarrow$  H<sub>2</sub>O process due to the strong \*OH adsorption strength. On the right-side, because of the weak adsorption for \*OOH, the process of generating \*OOH intermediates from oxygen becomes the limiting step. A similar volcano curve can be obtained by plotting the adsorption free energy of the \*OOH and the ORR overpotential, and the details are presented in Figure S7.

The d-band centers ( $\varepsilon_d$ ) were calculated to explain the interaction of the adsorbates with the adsorption sites because the O<sup>\*</sup> adsorption strength of a metal is closely correlated with its d-orbital levels [39]. The d-band centers of the adsorption sites of Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> were calculated to explain the interaction of the \*O intermediate with the adsorption sites. As shown in Figure 7a, there is no linear relationship between the adsorption energy of the \*O intermediate and the d-band center of the adsorption site. A small deformation of the geometry of the metal cluster was caused by O adsorption. The adsorption energy was thought to be the superposition of the metal cluster's geometry deformation energy and the binding energy between the metal cluster and the O. The adsorption energy was decomposed as follows:  $\Delta E_{ads} = \Delta E_{deformation} + \Delta E_{binding}$ , where  $\Delta E_{deformation}$  is the difference in the energy of the metal cluster before and after the O adsorption;  $\Delta E_{binding}$  is the binding energy of the O on the metal cluster. A linear relationship between the binding energy and the d-band center is presented in Figure 7b. The adsorption strength of the adsorbed oxygen intermediate decreases with the downshift in  $\varepsilon_d$  to the Fermi energy level due to the d-p anti-bond orbital occupancy [39].



**Figure 6.** (a) Scaling relationships between the Gibbs free energy ( $\Delta G$ ) of \*OOH and \*OH for Ni<sub>6</sub>@M<sub>32</sub> and (b) for Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>. (c) The linear relationship between the ORR overpotential and \*OH adsorption free energy.

The PDOS was analyzed to explore the interaction between O<sup>\*</sup> and the active site, as presented in Figure 7c. The blue and green colors represent the d state distributions of the adsorption sites, and the red part represents the p-orbital distribution of the adsorbed oxygen atom. In the PDOS diagrams of Ni<sub>6</sub>@M<sub>32</sub> (M = Au, Ag) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Au, Ag), the antibonding orbitals are occupied, resulting in weakened adsorption strength. On the contrary, the PDOS diagrams of Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pt, Pd) show that the antibonding orbital energy levels shift up over the Fermi energy level, leading to a relatively stronger d-p interaction. Comparing Ni<sub>6</sub>@M<sub>32</sub> and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>, the single Pt atom causes the d-band centers to up-shift to the Fermi energy level, resulting in a slightly stronger adsorption interaction significantly improved the potential-limiting step \*O  $\rightarrow$  \*OH, with a reduced overpotential of  $\eta^{ORR} = 0.12$  V. Among all the candidates, Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> is a promising multifunctional electrocatalyst for splitting water ( $\Delta G_{TS}^{Heyrovsky} = 0.10$  eV and  $\eta^{OER} = 0.33$  V) and has a low overpotential of  $\eta^{ORR} = 0.21$  V.

In summary, the electronic properties of the adsorption sites can be manipulated by changing the chemical composition of the core and shell. The free energies and electronic structures of the core–shell  $Ni_6@Pt_1M_{32}$  nanoclusters can be modulated to offer improved performance in the electrocatalysis of the ORR, HER and OER. In the ORR,  $Ni_6@Pt_1Pd_{31}$  and  $Ni_6@Pt_1Ag_{31}$  exhibit lower overpotentials than Pt (111). In the HER,  $Ni_6@Cu_{32}$  (0.14 eV),  $Ni_6@Pt_1Cu_{31}$  (0.21 eV),  $Ni_6@Pt_1Pd_{31}$  (0.33 eV) and  $Ni_6@Pt_1Ag_{31}$  (0.10 eV) are promising efficient electrocatalysts. In the OER, the overpotentials of  $Ni_6@Pt_1Ag_{31}$  and  $Ni_6@Pt_1Au_{31}$  are lowered compared to that of Pt (111).



**Figure 7.** (a) Plot of the adsorption free energy of \*O on  $Ni_6@M_{32}$  and  $Ni_6@Pt_1M_{31}$  against the d-band center of the adsorption site. (b) Plot of the binding energy of \*O on  $Ni_6@M_{32}$  and  $Ni_6@Pt_1M_{31}$  against the d-band center of adsorption site. (c) Density of states projected onto the d states of adsorption site on \*O of  $Ni_6@M_{32}$  (blue), adsorption site on \*O of  $Ni_6@Pt_1M_{31}$  (green), and the p states of adsorbed oxygen atoms, respectively (pink).

## 3. Computational Details

# 3.1. Computational Methods

Spin-polarized DFT methods were implemented in the Vienna Ab initio Simulation Package (VASP) [40–42] to carry out energy calculations and a geometry optimization. The interaction between valence and core electrons was described using the projector-augmented wave (PAW) pseudopotential [43,44], with an energy cutoff for the plane waves of 400 eV. A generalized gradient approximation (GGA) with the PW91 functional was

used to calculate the exchange–correlation energies [45,46]. The clusters were placed at the center of a 20 × 20 × 20 Å<sup>3</sup> cubic box, 65% of which was vacuum space to avoid interaction between the clusters and their images. A Pt (111) slab was modeled using a five-layer, periodically repeated  $\sqrt{3} \times \sqrt{2}$  super cell with 35 Å of vacuum space. A Gamma (1 × 1 × 1) point mesh was used during the geometric optimization of clusters. A threshold for self-consistent calculations of 1 × 10<sup>-5</sup> eV was used, and 0.02 eV/Å was used for ionic optimization. The transition state (TS) was determined via the Dimer method [47]. A Bader charge analysis was conducted to analyze the charge transfer [48].

#### 3.2. Models

A truncated octahedral (TO) structure was employed as the theoretical model. The shell of the TO structure consists of eight (111) planes and six (100) planes. There are eight non-equivalent adsorption sites (two top sites, three bridge sites, two face sites and one hollow site) on the  $Pt_{38}$  and  $Ni_6@M_{32}$  (M = Pt, Pd, Cu, Ag, Au) clusters. The structures are shown in Figure 1.

# 4. Conclusions

A high-efficiency and low-cost multifunctional electrocatalyst for splitting water and reducing oxygen is required for the practical applications of regenerative fuel cells. The HER, OER and ORR activity trends were investigated for core–shell  $Ni_6@M_{32}$  (M = Pt, Pd, Cu, Ag, Au) and  $Ni_6@Pt_1M_{31}$  (M = Pd, Cu, Ag, Au) via first-principles calculations. The core-shell Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> clusters present abundant active sites with moderate adsorption strengths for \*H, \*O, \*OH and \*OOH. The HER reaction energy barriers and rate constants indicated that  $Ni_6@Pt_1Ag_{31}$  was the most efficient catalyst of all the  $Ni_6@M_{32}$  (M = Pt, Pd) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> clusters at an H coverage of  $\theta_{H^*} = 2/6$ . The Pt active site decreased the energy barrier and changed the reaction mechanism. The Volmer-Heyrovsky reaction mechanism was favorable for  $Ni_6@M_{32}$ , and the Volmer–Tafel process was a kinetically advantageous reaction pathway for Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub>. The ORR and OER overpotentials of  $Ni_6@Pt_1Ag_{31}$  were calculated to be 0.12 and 0.33 V, and the OER overpotential was lower than that of RuO<sub>2</sub> and IrO<sub>2</sub>, which proves that Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> is a promising multifunctional electrocatalyst for the OER, HER and ORR. The present work provides significant insights for further searches for a high-efficiency and low-cost multifunctional electrocatalyst for regenerative fuel cells.

Supplementary Materials: The following supporting information can be downloaded at: https://www.action.com/actionals //www.mdpi.com/article/10.3390/molecules28227563/s1, Figure S1: The relationship between the calculated average binding energy of catalysts and the amount of charge transfer between the core and shell (red represents the amount of Bader charge transfer, blue represents the average binding energy); Figure S2: Density of states projected onto the d states of Ni<sub>6</sub>@M<sub>32</sub> clusters (left) and  $Ni_6@Pt_1M_{31}$  (M = Pd, Cu, Ag, Au) clusters (right); Figure S3: The differential Gibbs free energy profiles  $(d - \Delta G_{H^*})$  over the Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag, Au) clusters (a,d,g,j,m), the average Gibbs free energy profiles ( $a - \Delta G_{H^*}$ ) (b,e,h,k,n), and the volcano plot of  $i_0$  as a function of  $d - \Delta G_{H^*}$  at the best H coverage (c,f,i,l,o) and the highlight in blue denotes the free energy window of  $\pm 0.25$  eV; Figure S4: Density of states projected onto the d states of adsorption sites of Ni<sub>6</sub>@Pd<sub>32</sub> clusters (left) and Ni<sub>6</sub>@Pt<sub>1</sub>Pd<sub>31</sub> clusters (right) under different hydrogen coverages; Figure S5: Insight into the electron density disparity at the solid-liquid interface in the initial state (Heyrovsky) is presented for the catalysts (a) 6H-Ni<sub>6</sub>@Pt<sub>1</sub>Pd<sub>31</sub>, (b) 4H-Ni<sub>6</sub>@Pt<sub>1</sub>Cu<sub>31</sub>, (c) 2H-Ni<sub>6</sub>@Pt<sub>1</sub>Ag<sub>31</sub> and (d) 2H-Ni<sub>6</sub>@Pt<sub>1</sub>Au<sub>31</sub>. Regions of electron depletion and electron accumulation are depicted in cyan and light yellow, respectively; Figure S6: The potential energy profiles of the HER by Volmer-Tafel process and Volmer-Heyrovsky process at the optimal coverage of H. (a,b) Ni<sub>6</sub>@Pt<sub>32</sub>, (c,d) Ni<sub>6</sub>@Pd<sub>32</sub>, (e,f) Ni<sub>6</sub>@Cu<sub>32</sub>, (g,h) Ni<sub>6</sub>@Ag<sub>32</sub>, respectively; Figure S7: The linear relationship between ORR overpotential and \*OOH adsorption free energy of catalysts according to four-electron step mechanism (ORR volcano plot); Table S1: The models by doping a Pt atom at the core  $(Ni_5Pt_1@M_{32})$ , the center or the hexagonal  $(Ni_6@Pt_1M_{31})$  site of the surface in the core-shell nanocluster  $Ni_6@M_{32}$  (M = Pd, Cu, Ag, and Au); Table S2: Structural parameters of core-shell cluster catalysts; Table S3: The optimal  $|d-\Delta G_{H^*}|$  and

 $|a-\Delta G_{H^*}|$  and  $log(i_0)$  values of Ni<sub>6</sub>@M<sub>32</sub> (M = Pt, Pd, Cu, Ag, Au) and Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Pd, Cu, Ag, Au) and corresponding Bader charge of hydrogen atom; Table S4: The most stable adsorption sites and corresponding adsorption free energies of O, OH and OOH intermediates on the catalysts; Table S5: The reaction free energy corresponding to the four-electron step of the ORR reaction on the catalyst and the overpotential of the ORR and OER reactions; Table S6: The average binding energy of Ni<sub>6</sub>@M<sub>32</sub> (M = Ni, Pt, Pd, Cu, Ag, Au); Table S7: The formation energy of Ni<sub>6</sub>@Pt<sub>1</sub>M<sub>31</sub> (M = Ni, Pd, Cu, Ag, Au); Table S8: Alteration in energy accompanying the migration of two hydrogen atoms from distinct adsorption sites (either on the same or different facets) on Ni<sub>6</sub>@Cu<sub>32</sub> to a unified adsorption configuration; Text S1: Supplementary information for computational design of Ni<sub>6</sub>@Pt1M31 clusters for multifunctional electrocatalysts. References [37,49–53] are cited in the supplementary materials.

**Author Contributions:** Conceptualization, D.T.; methodology, D.T. and J.J.; software, D.T. and J.J.; validation, D.T. and J.J.; formal analysis, D.T. and J.J.; investigation, J.J.; resources, D.T.; data curation, D.T. and J.J.; writing—original draft preparation, J.J.; writing—review and editing, D.T. and J.J.; visualization, J.J.; supervision, D.T.; project administration, D.T.; funding acquisition, D.T. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Nature Science Foundation of China (91961204).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Acknowledgments: The authors acknowledge the Supercomputer Center of Dalian University of Technology for providing computation resources.

**Conflicts of Interest:** The authors declare no conflict of interest.

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