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## Research Article

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# Fullerene-hosted nickel clusters as electrocatalysts for efficient overall water splitting: activity and mechanism study

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## Abstract

The design of highly efficient catalysts for water splitting (WS) is a pivotal approach to the search for sustainable energy conversion technologies. WS consists of two fundamental half-reactions, including the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), each necessitating electrocatalysts that exhibit both superior activity and long-term stability. Building upon a recent discovery of nickel clusters anchored at NiN<sub>3</sub> centers and their demonstrated efficacy in the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) (Angew. Chem. Int. Ed. 2025, 64, e202424552), we report, for the first time, a density functional theory (DFT) investigation of the OER and HER pathways on NiN<sub>3</sub> sites as well as Ni<sub>6</sub>-NiN<sub>3</sub> clusters incorporated within a C<sub>60</sub> fullerene framework (NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub>). The primary aim of this study is to elucidate the electrocatalytic performance of NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> systems toward OER and HER. Among the investigated substrates, Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> demonstrates the best thermodynamic performance for hydrogen adsorption ( $\Delta G_H = -0.10$  eV), highlighting its enhanced catalytic suitability for the HER relative to the NiN<sub>3</sub>@C<sub>60</sub> counterpart. Computational results further demonstrate that Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> exhibits superior catalytic activity in OER, achieving a reduced overpotential ( $\eta^{\text{OER}} = 0.68$  V) compared to NiN<sub>3</sub>@C<sub>60</sub>.

**Keywords:** Hydrogen evolution reaction; Oxygen evolution reaction; water-splitting; Fullerene.

## 1. Introduction

The catalysis of the oxygen and hydrogen evolution reactions (OER and HER) introduces an efficient strategy to energy challenges [1-3]. Pt-based electrocatalysts show excellent activity and stability, but designing inexpensive electrocatalysts remains a major research area [4-7]. The exploration of earth-abundant transition metal-based catalysts, such as those derived from Fe, Co, Ni, and Mn, has emerged as a promising alternative to Pt-based systems [8, 9]. These materials often exhibit favorable electronic structures and tunable coordination environments that facilitate the adsorption and desorption of reaction intermediates. Furthermore, single-atom catalysts (SAC) and heteroatom-doped carbon supports have demonstrated remarkable activity by maximizing atomic utilization and tailoring the local electronic density of states [10]. Moreover, nanostructuring strategies, including the design of core-shell architectures, defect engineering, and interface modulation, have been shown to enhance catalytic performance by increasing active site exposure and improving charge transfer kinetics [11, 12]. Despite these advances, challenges remain in achieving long-term stability under various electrochemical conditions, as well as in scaling up synthesis methods for practical applications. Addressing these issues requires a feasible approach that integrates mechanistic understanding, advanced characterization techniques, and sustainable material design principles. Catalysts with transition metal-nitrogen-carbon (TM-N-C) active sites have been previously introduced as alternatives to Pt-based electrocatalysts for OER and HER [13-15]. The TM atoms embedded in the carbon-nitrogen centers of catalysts perturb the electron density at the active sites [16, 17]. Basically, TM-N-C active sites in electrocatalysts can efficiently interact with the intermediates of OER and HER [18-21]. Besides, the geometry of the transition metals in TM-N-C centers of catalysts can remarkably impact the OER and HER mechanisms [22-26]. Furthermore, the electronic coupling between TM-N-C frameworks plays a

decisive role in modulating the adsorption energies of key intermediates, such as \*OH, \*O, and \*OOH in OER, and \*H in HER [27, 28]. This coupling not only optimizes the binding strength of intermediates but also enhances charge transfer efficiency across the electrode-electrolyte interface [29-31]. From a mechanistic perspective, the coordination number and oxidation state of the transition metal centers mainly determine the reaction pathway, influencing whether the OER proceeds via a four-electron mechanism [30]. Similarly, in HER, the balance between Volmer, Heyrovsky, and Tafel steps is strongly affected by the local geometry and electronic configuration of TM-N-C sites [31]. In a recent and fascinating finding, the use of Ni clusters located at Ni-N<sub>3</sub>-C active sites as electrocatalysts for efficient CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) has been investigated [32]. The results show that locating Ni<sub>6</sub> clusters can considerably stabilize the Ni-N<sub>3</sub> active sites (Ni<sub>6</sub>/NiN<sub>3</sub>), leading to highly efficient CO<sub>2</sub>RR catalysis. While Ni<sub>6</sub>/NiN<sub>3</sub> clusters have been previously explored in the context of CO<sub>2</sub>RR, investigations into their applicability as electrocatalysts for the OER and HER in water-splitting remain limited. Motivated by this noteworthy observation, we seek to determine whether embedding NiN<sub>3</sub> and Ni<sub>6</sub>/NiN<sub>3</sub> centers within a C<sub>60</sub> fullerene framework (NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub>) can facilitate the catalytic performance of HER and OER.

## 2. Computational details

Using the GAUSSIAN09 program [34], density functional theory (DFT) computations were carried out at the Perdew-Burke-Ernzerhof (PBE) functional [33] combined with the def2-TZVP basis set. Long-range dispersion interactions were taken into account through the application of Grimme's D3 correction scheme [35]. A systematic evaluation was conducted on the catalytic performance of NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> for the OER in WS. The OER is generally understood to follow a pathway involving the sequential formation of adsorbed intermediate species on the catalyst surface, in line with the mechanistic description put forward by Nørskov [36]:





where  $*O$ ,  $*OH$ , and  $*OOH$  correspond to intermediates adsorbed on the  $NiN_3@C_{60}$  and  $Ni_6/NiN_3@C_{60}$  substrates. Besides, the  $\Delta G$  values are calculated according to the subsequent expression [37, 38]:

$$\Delta G_i = E_{ads} + \Delta ZPE - T\Delta S - e\phi \quad (5)$$

$$\Delta G_1 = E_{*-OH} - E_* - E_{H_2O} + \frac{1}{2}E_{H_2} + \Delta ZPE - T\Delta S - eU - K_B T \ln 10 \times pH \quad (6)$$

$$\Delta G_2 = E_{*-O} - E_{*-OH} + \frac{1}{2}E_{H_2} + \Delta ZPE - T\Delta S - eU - K_B T \ln 10 \times pH \quad (7)$$

$$\Delta G_3 = E_{*-OOH} - E_{*-O} - E_{H_2O} + \frac{1}{2}E_{H_2} + \Delta ZPE - T\Delta S - eU - K_B T \ln 10 \times pH \quad (8)$$

$$\Delta G_4 = E_* - E_{*-OOH} + 2E_{H_2O} + \frac{3}{2}E_{H_2} + 4.92 + \Delta ZPE - T\Delta S - eU - K_B T \ln 10 \times pH \quad (9)$$

where  $E_{ads}$ , is defined as the adsorption energy,  $\Delta ZPE$  is the correction for zero-point energy,  $T\Delta S$  represents the entropy term,  $e$  is the charge of an electron, and  $\phi$  refers to the applied potential relative to the normal hydrogen electrode. The oxygen evolution reaction overpotential ( $\eta^{OER}$ ) can also be computed using [37, 38]:

$$\eta^{OER} = \frac{\max\{\Delta G_i\}}{e} - 1.23 \quad (10)$$

In this context, the term  $\max\{\Delta G_i\}$  refers to the largest Gibbs free energy variation obtained from the set of values derived using Eqs. (6-9). It is important to note that as the overpotential for the OER approaches zero. indicating a smaller value, the electrocatalytic activity becomes more favorable. Following this, a thorough assessment was carried out to evaluate the HER performance of the  $NiN_3@C_{60}$  and  $Ni_6/NiN_3@C_{60}$  catalytic surfaces. Following the model developed by Nørskov *et. al.* [36], we calculated the  $\Delta G_H^*$  as a key metric for evaluating HER performance.

Near-zero  $\Delta G_H^*$  values are desirable, as they indicate an ideal thermodynamic equilibrium between the adsorption and desorption of hydrogen at the active sites, which is essential for optimal hydrogen evolution.

### 3. Results and discussion

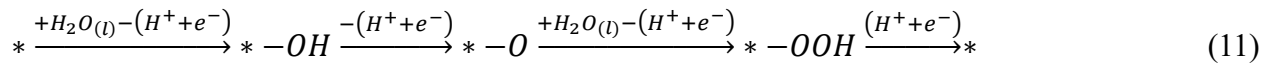
#### 3.1. $\text{NiN}_3@\text{C}_{60}$ and $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$ substrates

To identify the most energetically favorable geometries of  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$ , structural optimizations were carried out. The resulting equilibrium structures are presented in Fig. 1. Throughout the optimization process, no symmetry restrictions were imposed, and both systems,  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$ , were allowed to relax completely without any constraints. The calculated bond distances of Ni-N and Ni-C in the  $\text{NiN}_3@\text{C}_{60}$  are 2.07 Å and 1.95 Å, respectively. Our calculations revealed that the Ni-N distance in  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  (2.05 Å) is slightly smaller than this value in the  $\text{NiN}_3@\text{C}_{60}$  system (2.07 Å). The calculated Ni-Ni bond lengths in  $\text{Ni}_6$  cluster located at the  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  are about 2.32 Å, aligning with recent findings on  $\text{Ni}_6/\text{NiN}_3$  clusters [32]. Fig. 1 shows the molecular electrostatic potential (MEP) analysis of the considered  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  systems. The molecular electrostatic potential maps reveal electron-deficient regions in blue and electron-rich regions in red. In the studied systems, electron depletion is primarily localized around the Ni atoms, while electron accumulation occurs on the fullerene  $\text{C}_{60}$  framework. The strong positive electrostatic potential (blue) surrounding the Ni active sites indicates a high tendency to attract intermediates involved in the OER. Natural bond orbital (NBO) analysis further supports this observation, showing charge transfer from Ni atoms to neighboring nitrogen and carbon atoms. Among the considered systems,  $\text{NiN}_3@\text{C}_{60}$  displays the highest positive charge on its Ni center (+1.225|e|), higher than that of  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  (+1.180|e|). The NBO charge distribution aligns well with the electrostatic potential maps observed in the MEP analysis.

(Fig. 1). The binding strength of OER intermediates depends on the charge state of the catalytic sites [39]. Therefore, if Ni centers possess a slightly lower positive charge, they are likely to improve catalytic performance by mitigating overly strong adsorption. To further explore the influence of NiN<sub>3</sub> and Ni<sub>6</sub>/NiN<sub>3</sub> centers on the electronic structure of C<sub>60</sub>, we calculated the density of states (DOS) for each system (Fig. 2). The results indicate that the HOMO-LUMO energy gap (E<sub>HLG</sub>) of NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> clusters varies depending on the nature of the incorporated Ni centers. Specifically, NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> exhibit semimetallic character, with E<sub>HLG</sub> values of 0.02 eV and 0.06 eV, respectively. DOS profiles further reveal that, in the NiN<sub>3</sub>@C<sub>60</sub> system, the HOMO shifts to lower energies while the LUMO shifts to higher energies, thereby increasing the E<sub>HLG</sub> relative to Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub>. These observations are consistent with the recent findings of Zhang *et al.* [32] on Ni<sub>6</sub>/NiN<sub>3</sub> clusters. Frontier molecular orbital (FMO) analysis (Fig. 2) shows that the HOMO and LUMO of NiN<sub>3</sub>@C<sub>60</sub> are predominantly localized on the NiN<sub>3</sub> center, whereas in Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> they are mainly distributed around the Ni<sub>6</sub> cluster anchored to the fullerene framework.

### 3.2. OER activity of NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> substrates

We systematically evaluate the OER catalytic performance of NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> in water splitting. Following the approach of Nørskov [36], the catalytic process is described in terms of a thermodynamically viable series of elementary steps involving intermediate adsorption on the catalyst surface:



As outlined in Eq. (11), the oxygen evolution reaction on the substrate follows a four-step mechanism. It begins with the adsorption and dissociation of H<sub>2</sub>O, generating a hydroxyl intermediate and a proton-electron pair. The \*OH species is then deprotonated, resulting in an

adsorbed oxygen atom. In the third step, the  $^*O$  intermediate reacts with another  $H_2O$  molecule to generate a hydroperoxyl species ( $^*OOH$ ), accompanied by the release of an additional  $e^-/H^+$  pair. In the last step,  $^*OOH$  decomposes to release  $O_2$  and another proton-electron pair. So, we systematically investigated the OER intermediates adsorption on  $NiN_3@C_{60}$  and  $Ni_6/NiN_3@C_{60}$ . The Ni atoms in both clusters act as the active sites, showing the highest affinity for intermediate adsorption. Optimized geometries of the adsorbed  $^*OH$ ,  $^*O$ , and  $^*OOH$  species are shown in Fig. 3, and their corresponding adsorption energies are provided in Fig. 4. Among the studied clusters, the adsorption energies exhibit clear trend,  $^*O$  intermediates show the highest binding strength, while  $^*OOH$  species are characterized by the lowest. Among the studied systems,  $Ni_6/NiN_3@C_{60}$  displays the weakest  $E_{ads}$  values for O and OH, while  $NiN_3@C_{60}$  demonstrates the strongest adsorption for all three intermediates. This difference stems from the distinct atomic charges at the Ni sites, including the Ni atom in  $Ni_6/NiN_3@C_{60}$  has a reduced positive charge ( $+1.180|e|$ ), lowering the adsorption energies for  $^*O$  and  $^*OH$  species. In contrast, the higher positive charge ( $+1.225|e|$ ) on the Ni atom in  $NiN_3@C_{60}$  enforces stronger intermediate-substrate binding, which suppresses  $O_2$  desorption and thus lowers catalytic efficiency. The calculated  $\Delta G$  corresponding to the OER steps are gathered in Table 1. Table 2 and Fig. 5 also listed the parameters used to compute these  $\Delta G_i$  values. The potential-determining step (PDS) in the OER mechanism corresponds to  $\Delta G_4$  for both  $NiN_3@C_{60}$  and  $Ni_6/NiN_3@C_{60}$  substrates, with values of 2.22 eV and 1.91 eV, respectively. A key finding is that  $Ni_6/NiN_3@C_{60}$  outperforms  $NiN_3@C_{60}$  in OER activity, a difference that arises from the diminished positive charge carried by the Ni center in the former system. Consequently, this reduced positive charge reduces both the Gibbs free energy barrier of the PDS and the overpotential. The calculated  $\eta^{OER}$  follow the sequence  $NiN_3@C_{60} >$

Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub>. In line with earlier discussion, a lower  $\eta^{\text{OER}}$  indicates enhanced catalytic activity, which certainly impacts both the OER and the broader water-splitting application.

### 3.3. HER activity of the NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub>

Previous experimental and theoretical studies have revealed that  $\Delta G_{\text{H}}^*$  is a key descriptor for evaluating HER activity [40-42]. A largely positive  $\Delta G_{\text{H}}^*$  reflects weak hydrogen binding, which limits reaction kinetics, while a large negative  $\Delta G_{\text{H}}^*$  indicates excessively strong adsorption, hindering the desorption step and diminishing overall HER efficiency. Thus, optimal HER catalysis occurs as  $\Delta G_{\text{H}}^*$  tends to zero, indicating balanced thermodynamics between hydrogen adsorption and desorption that supports superior activity [43]. Accordingly, the HER performance of the examined substrates is assessed by examining the reaction sequences, namely the Volmer-Heyrovský (VH) and Volmer-Tafel (VT) routes, given by Eqs. (12) and (13), respectively:



In both VT and VH mechanisms of the HER, the adsorption of hydrogen atoms represents the initial step, and the corresponding  $\Delta G_{\text{H}}^*$  is widely known as a fundamental quantity of catalytic activity [41, 42]. According to the Sabatier principle, an ideal HER electrocatalyst should exhibit a  $\Delta G_{\text{H}}^*$  value close to zero, reflecting a balanced interaction that is neither too weak to limit adsorption nor too strong to hinder hydrogen desorption [43]. The optimized adsorption geometries corresponding to the VH and VT pathways are presented in Fig. 6. A detailed examination of hydrogen binding sites on NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> shows that the NiN<sub>3</sub> motifs consistently serve as the most thermodynamically favorable locations for \*H adsorption, highlighting their

pivotal contribution to HER catalysis. Table 3 compiles the computed  $\Delta G_H^*$  values for both substrates, enabling a side-by-side comparison of their catalytic behavior. Our calculations reveal that all  $\Delta G_H^*$  values across the two pathways fall within a negative range of -0.10 to -0.19 eV, indicating that hydrogen uptake on these surfaces is both energetically downhill and kinetically accessible. Notably, the  $\Delta G_H^*$  values for  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  are closer to the optimal gap (-0.10 eV for the Volmer-Heyrovský route and -0.14 eV for the Volmer-Tafel route), reflecting a more favorable equilibrium between adsorption and desorption that increases overall catalytic effectiveness. In addition, under high hydrogen coverage conditions where H-H coupling is efficient, the Volmer-Heyrovský mechanism tends to be more favorable than the Volmer-Tafel pathway. Throughout our analysis,  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  consistently yields more desirable  $\Delta G_H^*$  values than its  $\text{NiN}_3@\text{C}_{60}$  counterpart, pointing to its strong potential as an HER catalyst. This behavior can be explained by differences in atomic charge: the Ni center in  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  bears a lower positive charge (+1.180|e|), which weakens  $^*\text{H}$  binding and thereby eases  $\text{H}_2$  evolution. In contrast, the Ni atom in  $\text{NiN}_3@\text{C}_{60}$  possesses a higher positive charge (+1.225|e|), leading to stronger substrate-intermediate interactions that hinder hydrogen desorption and reduce catalytic performance.

#### 4. Conclusions

This study presents the successful construction of a  $\text{Ni}_6/\text{NiN}_3$  active site embedded in a  $\text{C}_{60}$  fullerene framework, which serves as an electrocatalyst exhibiting remarkable performance for both the oxygen evolution reaction and the hydrogen evolution reaction. Using density functional theory calculations, the  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  systems were thoroughly characterized in terms of their structural and electronic properties. Among these two configurations,  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  emerged as the superior HER catalyst, outperforming  $\text{NiN}_3@\text{C}_{60}$  by achieving an exceptionally

low overpotential ( $\Delta G_H^* = -0.10$  eV). A systematic analysis was further carried out to link the electronic features of the systems with their OER activity, establishing clear rational trends between the binding energies of the key intermediates (\*OH, \*O, and \*OOH) and the overall catalytic efficacy. Through computation of the Gibbs free energy variations associated with the individual OER half-reactions, Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> was identified as a highly promising substrate, characterized by a low overpotential of 0.68 V.

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**Funding Declaration**

Not applicable

**Conflicts of interest**

There are no conflicts to declare.

**Data availability statement**

The data that supports the results of this study are available on a reasonable request from the corresponding author.

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**Table 1.** The  $\Delta G_i$  and  $\eta^{OER}$  for OER process on the  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  substrates ( $U^0=1.23$  V).

| system                                   | $\Delta G_1(\text{eV})$ | $\Delta G_2(\text{eV})$ | $\Delta G_3(\text{eV})$ | $\Delta G_4(\text{eV})$ | $\eta^{OER}(\text{V})$ |
|------------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------------------------|
| $\text{NiN}_3@\text{C}_{60}$             | 0.57                    | 1.81                    | 0.31                    | 2.22                    | 0.99                   |
| $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$ | 1.02                    | 1.65                    | 0.33                    | 1.91                    | 0.68                   |

**Table 2.** The parameters employed in the  $\Delta G_i$  calculations of the OER on the  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  substrates.

| system                                   | Intermediates | Energy (eV) | ZPE (eV) | TS (eV) |
|------------------------------------------|---------------|-------------|----------|---------|
| $\text{NiN}_3@\text{C}_{60}$             | *OH           | -4298.61    | 0.42     | 0.13    |
|                                          | *O            | -4297.94    | 0.41     | 0.13    |
|                                          | *OOH          | -4373.76    | 0.43     | 0.13    |
| $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$ | *OH           | -4424.09    | 0.42     | 0.13    |
|                                          | *O            | -4423.43    | 0.41     | 0.13    |
|                                          | *OOH          | -4499.25    | 0.43     | 0.13    |

**Table 3.** Calculated  $\Delta G_H^*$  values for the Volmer- Heyrovsky and Volmer-Tafel mechanisms on the  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  substrates ( $U_0= 1.23 \text{ V}$ ).

| Substrate                                | Volmer- Heyrovsky   | Volmer-Tafel        |
|------------------------------------------|---------------------|---------------------|
|                                          | $\Delta G_H^*$ (eV) | $\Delta G_H^*$ (eV) |
| $\text{NiN}_3@\text{C}_{60}$             | -0.15               | -0.19               |
| $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$ | -0.10               | -0.14               |

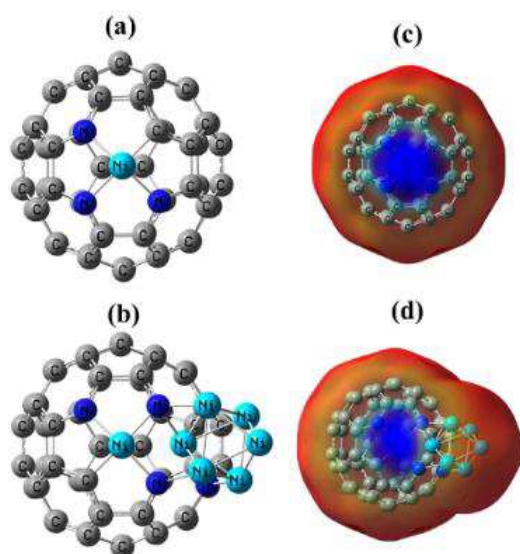


**Fig. 1.** The most stable geometries of (a)  $\text{NiN}_3@C_{60}$  and (b)  $\text{Ni}_6/\text{NiN}_3@C_{60}$  substrates. The molecular electrostatic potential maps (c and d) are also shown.

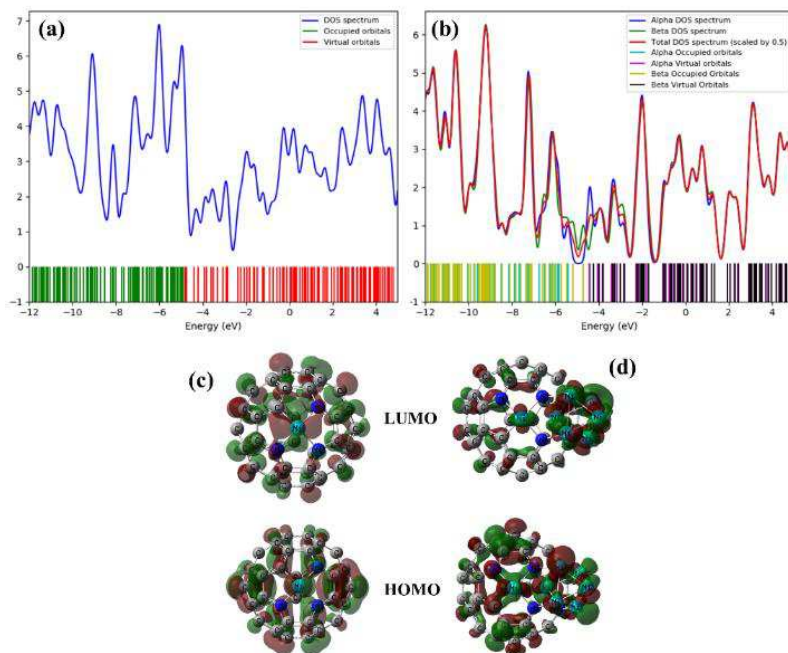


**Fig. 2.** The DOS profiles of (a)  $\text{NiN}_3@\text{C}_{60}$  and (b)  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  systems. The FMO analysis (c and d) are also shown.

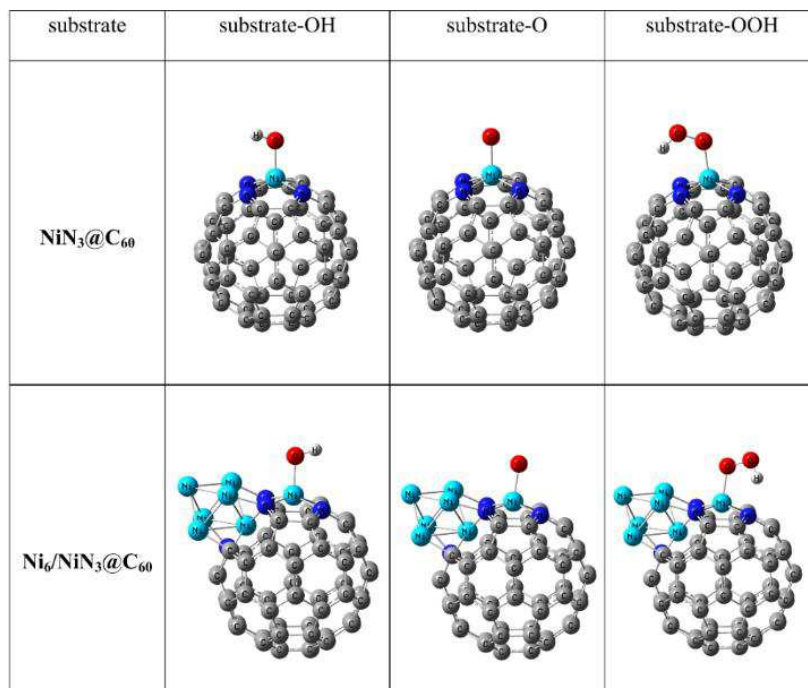


**Fig. 3.** Optimized stable geometries of OER intermediates adsorbed on  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  substrates.

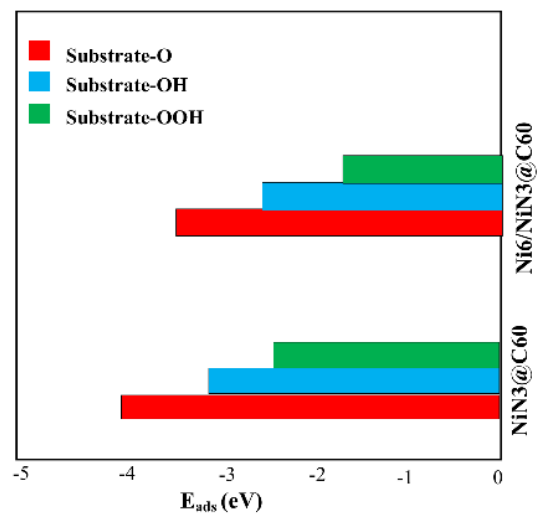


**Fig. 4.** Calculated adsorption energies of OER intermediates on NiN<sub>3</sub>@C<sub>60</sub> and Ni<sub>6</sub>/NiN<sub>3</sub>@C<sub>60</sub> substrates.

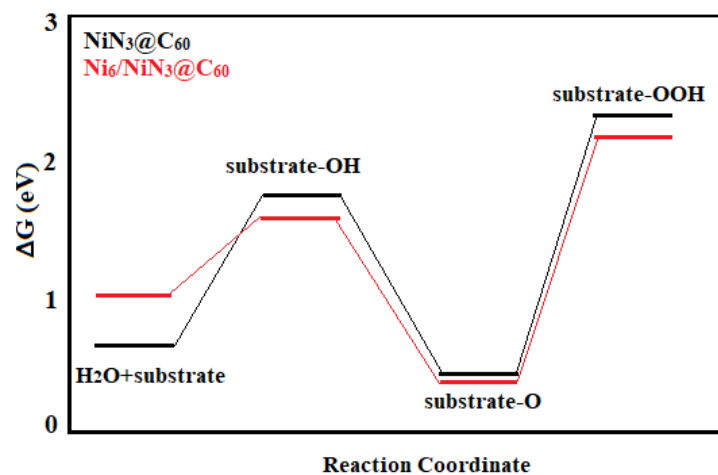


**Fig. 5.** Comparative evaluation of the Gibbs free energy changes for the OER on  $\text{NiN}_3@\text{C}_{60}$  and  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  substrates.

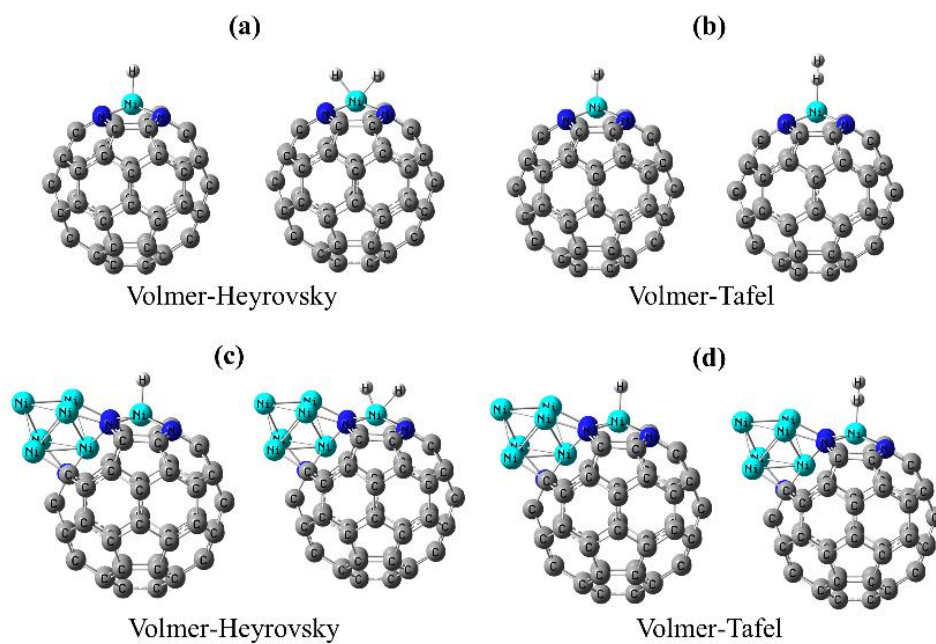


**Fig. 6.** The most stable geometries of intermediates in the Volmer-Heyrovsky and Volmer-Tafel mechanisms adsorbed on (a and b)  $\text{NiN}_3@\text{C}_{60}$  and (c and d)  $\text{Ni}_6/\text{NiN}_3@\text{C}_{60}$  substrates.