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Theoretical insight into the roles of cocatalysts in the Ni–NiO/ β -Ga₂O₃ photocatalyst for overall water splitting†

Taifeng Liu,^{ab} Ionut Tranca,^c Jingxiu Yang,^{ab} Xin Zhou^{*a} and Can Li^{*a}

The formation and stability of Ni_n and (NiO)_n ($n = 1-4$) clusters on the β -Ga₂O₃ surface have been studied by means of first-principles density functional theory calculations. It is found that the optimum interaction of the Ni_n and (NiO)_n clusters with the surface requires different surface sites. This optimizes the formation of interfacial bonds between the atoms from clusters and the coordinatively unsaturated atoms from the surface. The stability of the adsorbed Ni clusters increases with the number of Ni atoms. In a Ni_n/Ga₂O₃ system, as the Ga unoccupied states overlap with the unoccupied Ni state, the excited electrons transferred from Ga to Ni participate in the proton reduction reaction. Our calculations show that (NiO)_n clusters strongly adsorb on the Ga₂O₃ surface due to the negative adsorption energies within -1.9 eV to -3.7 eV. For (NiO)_n/Ga₂O₃, occupied states from the (NiO)_n cluster may accept the holes from O atoms in the Ga₂O₃ surface to take part in the photocatalytic water oxidation reaction.

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1. Introduction

Photocatalytic overall splitting of water over semiconductors has drawn great attention as one of the possible strategies for environmental remediation and energy conversion.^{1–5} Generally, a heterogeneous photocatalytic system is composed of a semiconductor and cocatalysts.⁶ The semiconductor is responsible for harvesting light, while photocatalytic reactions take place on cocatalysts loaded on the semiconductor. Cocatalysts can not only serve as reaction sites and catalyze reactions, but also promote the charge separation and transport driven by junctions/interfaces formed between the cocatalyst and light harvesting semiconductor.⁷ Many research studies show that loading suitable cocatalysts can significantly increase the photocatalytic activities of hydrogen and oxygen evolution reactions.^{8–12} Typically, the cocatalyst is a noble metal for reduction reactions (such as Pt, Pd, Ru, Rh and Au) or transition-metal oxide for oxidation reactions (such as CoO_x, NiO_x, IrO₂, MnO_x and RuO₂).

Nickel oxide has often been employed in many photocatalytic systems for water splitting,³ such as Ga₂O₃,^{13,14} SrTiO₃,^{15–17} La:KTaO₃,¹⁸ K₄Nb₆O₁₇,¹⁹ and Ba₅Nb₄O₁₅.²⁰ In

general, the pretreatment of H₂ reduction and subsequent O₂ oxidation is indispensable for nickel oxide loaded photocatalysts to show high activities. So the pretreated nickel oxide cocatalyst is often denoted as NiO_x in the literature.^{13–20} Ga₂O₃, as a representative of semiconductors with a d¹⁰ electronic configuration, exhibits high photocatalytic activity for water splitting.^{13,14} The results reported by Yanagida *et al.* show that only H₂ production was observed when Ga₂O₃ was used as the photocatalyst without NiO_x loading, and the activity was relatively low.¹³ A recent study showed that NiO_x loading is necessary to induce the stoichiometric formation of H₂ and O₂ by photocatalytic decomposition of water on Ga₂O₃ with tunable α - β phase junctions.¹⁴

Cocatalysts are typically present as nanoparticles on the semiconductor surface loaded by impregnation or *in situ* photo-deposition.²¹ The structural complexity of the nano-sized metal or metal oxide clusters on semiconductor surfaces makes it difficult to obtain structural and electronic information of these systems even under well-defined experimental conditions. Theoretical studies based on first-principles electronic structure calculations have proven to be useful for complementing the experimental results to illuminate the relationship between the surface structure and the physical and chemical properties of semiconductors, and further to understand the mechanism of the photocatalytic reaction.^{22–30}

Although experimental observations indicate that cocatalysts play an important role in promoting charge separation and increasing activity in photocatalytic systems, several critical questions on cocatalysts are still open. For example, how and where does a cocatalyst locate on the surface of semiconductors? How does the adsorption of the cocatalyst affect

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the electronic properties of photocatalysts? Why does loading cocatalysts promote the charge separation? To answer these questions, we took the Ni–NiO/ β -Ga₂O₃ photocatalytic system as a model and performed detailed theoretical calculations. In the present work, we computed the surface structures and formation energies of five different surfaces of β -Ga₂O₃, determined the stable configurations of Ni_{*n*} and (NiO)_{*n*} (*n* = 1–4) clusters adsorbed on the most stable surface of β -Ga₂O₃, and investigated the electronic properties and charge distribution for these systems. We found that small Ni_{*n*} and (NiO)_{*n*} clusters tend to form on different sites of the surface. The electronic structure analyses indicate that Ni_{*n*}/Ga₂O₃ systems participate in the photocatalytic hydrogen evolution reaction (HER) while (NiO)_{*n*}/Ga₂O₃ systems tend to take part in the photocatalytic oxygen evolution reaction (OER).

2. Computational details

All the DFT spin-polarized calculations were performed with the VASP (Vienna Ab initio Simulation Package) code.^{31,32} The exchange–correlation potential was described through the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation formalism.³³ The projector-augmented wave method was applied to describe electron–ion interactions.^{34,35} A Hubbard *U* term acting on the Ni 3d orbitals was added to the standard PBE functional employing the rotationally invariant formalism developed by Dudarev *et al.*,³⁶ in which only the difference ($U_{\text{eff}} = U - J$) between the Coulomb *U* and exchange *J* parameters is considered. In the present work, a value of $U_{\text{eff}} = 5.3$ eV was used, which was calculated self-consistently by Ferrari *et al.*³⁷ and which is in the range of 5–6 eV interval found in the literature.^{36,38,39}

Among the five different crystalline structures of Ga₂O₃, β -Ga₂O₃ is the most stable crystal phase.⁴⁰ This crystal phase exhibits excellent photocatalytic activity,^{41,42} and it is the subject of extensive experimental and theoretical studies.^{43–49} So in this work, we chose β -Ga₂O₃ to represent the semiconductor in photocatalytic systems. Full optimization of the cell parameters for the bulk β -Ga₂O₃ with a monoclinic structure (Fig. 1(a)) was carried out by using the $3 \times 11 \times 7$ Monkhorst–Pack type *k*-point sampling. The cutoff energy for the plane wave basis set was fixed at 520 eV. The calculated lattice parameters, $a = 12.504$ Å, $b = 3.101$ Å, $c = 5.915$ Å, and $\beta = 103.71^\circ$, are in good agreement with the experimental data.⁵⁰ For all the surface calculations a vacuum layer of 15 Å was used in order to avoid the interaction between periodic slabs. For the calculation of the surface energy, (1×1) cells were considered, a Monkhorst–Pack set of $3 \times 3 \times 1$ *k*-points was applied and all the atomic layers in the slabs were allowed to relax. During the optimization of the surfaces covered with adsorbates, a (3×2) supercell including a cell composition (Ga₂O₃)₂₄ was used. The upper half of the slab and the adsorbates were allowed to relax, while the bottom half of the slab was fixed at its optimized bulk position. Dipolar corrections were included along the axis normal to the surface. The geometries were considered to be converged when the forces on each ion were less than 0.01 eV Å^{−1}.

On top of the optimized geometries obtained at the GGA-PBE level, a more accurate approach, the hybrid HSE06 functional,^{51–53} was used to calculate the electronic properties for the most stable structures. This is necessary in order to achieve a good agreement between the experimental and the theoretical band gaps. The HSE06 functional includes a fraction α , of screened, short-range HF exchange to improve the derivative discontinuity of the Kohn–Sham potential for integer electron numbers. The percentage of HF exchange in a hybrid functional

Fig. 1 Illustration of bulk β -Ga₂O₃ crystal and stoichiometric surfaces: (a) bulk, (b) (100)-A, (c) (100)-B, (d) (001)-A, (e) (001)-B, and (f) (010). The red and brown balls stand for oxygen and gallium, respectively.

is not a universal constant and the optimal value can be system-dependent. The band gap of bulk β -Ga₂O₃ obtained from experiments was found to be in the range of 4.2–4.7 eV.^{14,33,54,55} In the present work, $\alpha = 0.3$ was used as this value can yield good agreement between the computed band gap (4.5 eV) and the experimental results.

3. Results and discussion

3.1. Bulk and surface properties

Fig. 1(a) shows that the unit cell of β -Ga₂O₃ contains four Ga₂O₃ formula units with two nonequivalent Ga sites and three nonequivalent O sites. Ga(I) is bonded to four O anions in the form of a distorted tetrahedron, while Ga(II) forms a highly distorted octahedron with six O anions. Each O(I) is threefold coordinated and shared by two octahedra and one tetrahedron. Each O(II) is also threefold coordinated and lies at the intersection of two tetrahedra and one octahedron. Each O(III) is fourfold coordinated and connected with three octahedra and one tetrahedron. The computed bond lengths are as follows: Ga(I)–O(I) = 1.864 Å, Ga(I)–O(II) = 1.867 Å, Ga(I)–O(III) = 1.894 Å, Ga(II)–O(I) = 1.969 Å, Ga(II)–O(II) = 1.951 Å, and Ga(II)–O(III) = 2.073 Å. All are in good agreement with the experimental values.⁵⁰

Five β -Ga₂O₃ surfaces of interest are created by cleaving the optimized bulk structure through the corresponding planes, and the resultant structures are depicted in Fig. 1(b–f). They are denoted as (100)-A, (100)-B, (001)-A, (001)-B and (010), respectively. Structural differences for these surfaces were intensively investigated by Bermudez.⁵⁶ In order to estimate the relative stability of these surfaces, slabs with different numbers of stoichiometric repeated layers were constructed for each surface. The computed total energies of the slabs, together with their corresponding numbers of Ga₂O₃ units, were then fitted into the following equation to calculate the surface formation energy γ ,

$$\gamma = (E_{\text{slab}} - nE_{\text{Ga}_2\text{O}_3})/2A \quad (1)$$

where E_{slab} is the total energy of the slab, n is the number of Ga₂O₃ units in the slab, and $2A$ is the total exposed area of the two identical sides of the slab.

As shown in Fig. 2, calculated surface energies are converged within 0.01–0.03 J m^{−2} for (100), (001) and (010) when n reaches 4, 8, and 10, respectively. The computed value of surface energy is 0.84 J m^{−2} for (100)-A, 0.47 J m^{−2} for (100)-B, 1.75 J m^{−2} for (001)-A, 1.18 J m^{−2} for (001)-B and 1.49 J m^{−2} for (010). Our results show that the (100)-B surface is the most stable one among the five surfaces we considered, which is in good agreement with available experimental and theoretical data.^{56–58} Therefore, we focus our calculations and discussions on the (100)-B surface in the following parts.

As shown in Fig. 1(c), the (100)-B surface is terminated by fivefold coordinated Ga(II) (Ga_{5c}(II)) and threefold coordinated O(III) (O_{3c}(III)). Ga(I) and O(I) atoms at the surface are fully coordinated, and there are no O(II) atoms in the surface plane. The side view of this surface is like a wave. The quadrilaterals composed of Ga_{5c}(II),

Fig. 2 Surface energies (in J m^{−2}) of fully optimized (100)-A, (100)-B, (001)-A, (001)-B and (010) surfaces of β -Ga₂O₃ as a function of the number n of stoichiometric repeated layers.

O_{3c}(III) and O(I) atoms are located in the wave crest, while Ga(I) atoms are situated in the wave trough. Based on the relaxed surface structure of (100)-B, total density of states (TDOS) and partial density of states (PDOS) have been evaluated by means of HSE06. As shown in Fig. 3, the valence band maximum (VBM) is mainly composed of O 2p states, slightly hybridized with Ga 3d and 4p states. Ga 4s states contribute more to the lower valence bands. The conduction band minimum (CBM) consists mostly of Ga 4s states. The valence bands exhibits the characteristic of mixed O 2p, Ga 4s, 4p and 3d states. The strong mixing of O and Ga orbitals is indicative of the high degree of covalent bonding in this semiconductor. The value of the band gap is computed to be 4.0 eV, which is smaller than that of the bulk (4.5 eV) due to the surface dangling bonds.

3.2. Formation of Ni_n clusters on the (100)-B surface of β -Ga₂O₃

To obtain the most stable structure for a given Ni_n ($n = 1$ –4) cluster supported on Ga₂O₃(100), the cluster was placed on the

Fig. 3 Density of states for the (100)-B surface of β -Ga₂O₃ calculated by HSE06. The Fermi level is shown through the vertical dashed line.

surface in all possible positions and in different orientations. The four most stable configurations for each $\text{Ni}_n/\text{Ga}_2\text{O}_3(100)$ are shown in Fig. 4, while the other configurations are summarized in the ESI (see Fig. S1†). Relative energies with respect to the

corresponding lowest-energy structures are shown in the figures. All of the obtained configurations show that after adding Ni_n clusters onto the surface, there are bonds formed between the cluster and surface, which are defined as

Fig. 4 Stable configurations of $\text{Ni}_n/\text{Ga}_2\text{O}_3(100)$ ($n = 1-4$) clusters (side and top views). Relative energies with respect to the corresponding lowest-energy structure are shown. Coloring scheme: red (surface O), brown (Ga) and blue (Ni). This color scheme applies to the following figure.

“interfacial bonds” in this work. This means that the interaction between clusters and the Ga_2O_3 surface belongs to the chemical adsorption. The adsorption energy, E_{ads} , of a cluster adsorbed on the $\beta\text{-Ga}_2\text{O}_3$ surface was defined as:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{cluster}} \quad (2)$$

where E_{total} is the total energy of the Ga_2O_3 surface with a cluster, E_{surface} is the total energy of the bare and relaxed surface, and E_{cluster} is the energy of the optimized cluster in the gas phase. To better understand the nucleation or growth of Ni_n clusters on the support, the average binding energy E_{binding} of Ni_n clusters adsorbed on the $\beta\text{-Ga}_2\text{O}_3$ surface was calculated as

$$E_{\text{binding}} = (E_{\text{total}} - E_{\text{surface}} - nE_{\text{Ni}})/n \quad (3)$$

where E_{Ni} is the energy carried by a free Ni atom in a vacuum.

The key structural parameters for the most stable configuration of each $\text{Ni}_n/\text{Ga}_2\text{O}_3(100)$ ensemble are displayed in Fig. 5. As shown in Fig. 5(a), the most stable adsorption site for an isolated Ni atom is in the middle of two nearest $\text{O}_{3\text{c}}(\text{III})$ atoms with an adsorption energy of -2.16 eV, resulting in two Ni–O bonds with an equal bond length of 1.856 Å, and the distance of $\text{Ga}_{5\text{c}}(\text{II})$ and the Ni atom to be 2.289 Å. The adsorption of the Ni atom increases the distance between the $\text{O}_{3\text{c}}(\text{III})$ atom and $\text{Ga}_{5\text{c}}(\text{II})$ atom by about 0.58 Å compared with the value for a clean surface. The adsorption of the Ni monomer induces therefore significant surface modifications. We have tested the adsorption of a single Ni atom on top of a single $\text{O}(\text{III})$ or $\text{O}(\text{I})$ atom. In the optimized structure, the Ni atom migrated to the bridge position, which is the same as the most stable structure. This means that the Ni atom prefers a bridge adsorption between two oxygens instead of a top one on the surface oxygen atom. Comparing the relative energies of all $\text{Ni}_1/\text{Ga}_2\text{O}_3$ optimized configurations from Fig. 4, one can notice that the formation of interfacial bonds between the Ni atom and the coordinatively saturated gallium/oxygen atoms from the surface

leads to less stable structures. Only the structure with the Ni binding to the $\text{O}(\text{III})$ and $\text{Ga}(\text{II})$ is stable, as it brings the three surface atoms to a coordination number similar to that in bulk Ga_2O_3 .

When a Ni_2 dimer is adsorbed on the $\text{Ga}_2\text{O}_3(100)$ surface, the most energetically favorable configuration is the horizontal adsorption (see Fig. 4), with an adsorption energy of -2.47 eV. The two Ni atoms are symmetrically located on the surface, forming six interfacial bonds. Owing to the adsorption of the additional Ni atom, the already bonded Ni atom is lifted and the bond length of Ni–O is computed to be 2.032 Å ($+0.18$ Å compared with the Ni–O bond from $\text{Ni}/\text{Ga}_2\text{O}_3(100)$). Similarly, the Ga–Ni bond is also lengthened by 0.25 Å. The calculated distance between the two Ni atoms is 2.429 Å, which is longer than that within the Ni_2 cluster in the gas phase by 0.065 Å. As shown in Fig. S1,[†] like in the case of the Ni monomer, more bond formation between the Ni_2 cluster and the fully saturated Ga and O atoms from the surface lead to less favorable structures. The average binding energy of the most stable structure is calculated to be -2.20 eV, which suggests that the addition of the second Ni atom slightly improves the stability of the first Ni atom.

There are two stable configurations for the isolated Ni_3 ternary cluster: the regular triangular form and the beeline form, and the latter is calculated to be more stable than the former by 0.12 eV. These two initial structures of the Ni_3 cluster were attached to the surface in different directions and positions. After optimization, some original linear configurations are curled (see structures i and k in Fig. S1[†]). Our calculations show that the total energy of the triangular configurations is always lower than that of the linear ones. For the lowest-energy structure (see Fig. 4 and 5(c)), one Ni atom is located in the most stable adsorption site for single Ni atom attached to the surface, and the other two Ni atoms symmetrically form bonds with $\text{O}(\text{I})$ atoms. The Ni– $\text{O}(\text{III})/\text{O}(\text{I})$ and Ni–Ni bonds are predicted to be 2.122 Å/ 2.008 Å and 2.336 – 2.400 Å, respectively. The Ni–Ni bonds within the triangular form are shorter and stronger than those in the adsorbed dimer. Corroborating this with the larger average binding energy for Ni_3 cluster on the surface (-2.28 eV), it suggests that the formation of the Ni_3 cluster is favorable on the surface.

The initial adsorption configurations for the Ni_4 cluster were set to be tetrahedral and rhombic. The tetrahedral structure is computed to be energetically more favorable than the rhombic one by 0.10 eV in the gas phase. Ten stable adsorption configurations were obtained after optimizations, as displayed in Fig. 4 and S1.[†] The results show that the adsorption of the tetrahedral Ni_4 cluster is energetically more favorable than that of the rhombic one. As shown in Fig. 5(d), the most stable configuration is generated by adding an extra Ni atom above the plane of the Ni_3 cluster in the lowest-energy structure of $\text{Ni}_3/\text{Ga}_2\text{O}_3(100)$. The introduction of the extra Ni atom decreases the average binding energy to -2.34 eV, and further improves the stability of the Ni_n cluster on the $\beta\text{-Ga}_2\text{O}_3$ surface. The Ni– $\text{O}(\text{I})/\text{O}(\text{III})$ and Ni–Ga bonds are calculated to be 1.95 Å/ 2.085 Å and 2.707 Å, respectively. The Ni–Ni bonds are in the range of 2.409 – 2.455 Å.

Fig. 5 Geometrical parameters for the most stable structures of $\text{Ni}_n/\text{Ga}_2\text{O}_3(100)$ ($n = 1$ – 4): (a) Ni , (b) Ni_2 , (c) Ni_3 , and (d) Ni_4 .

Our calculated results show that the addition of a new Ni atom to an existing Ni_n cluster adsorbed on the $\text{Ga}_2\text{O}_3(100)$ surface is energetically favorable. If the Ni_n cluster binds to coordinatively saturated Ga(I) atoms from the surface, the adsorption structure is energetically unfavorable. The average binding energy gradually decreases with the increase of n value in the Ni_n cluster, which indicates a tendency for this metal to aggregate on the surface. The most stable configuration of every Ni_n cluster ($n = 1-4$) indicates that one Ni cluster tends to form above Ga(I) atoms and between O(I) and $\text{O}_{3c(\text{III})}$ atoms.

To investigate the charge rearrangement upon the formed interface between the Ga_2O_3 surface and Ni_n cluster, Bader charge analysis has been performed.^{59,60} The optimized geometries of the surface with the adsorbed cluster, clean surface, and isolated cluster are kept fixed for the Bader charge analyses. The results shown in Table 1 demonstrate that when a Ni_n cluster is adsorbed onto the $\beta\text{-Ga}_2\text{O}_3(100)$ surface, it will lose electrons and carry some positive charge. It is interesting to note that for the three-dimensional Ni_4 cluster adsorbed system, only the Ni atoms bonded to the surface donate electrons to the surface, while the Ni atom at the top of the tetrahedron is nearly neutral, which indicates that at low metal coverage, the nickel adatom is ionic because it is directly bonded to surface oxygen; with the increase of the coverage, the newly arrived nickel adatoms are neutral unless they are bonded to the surface atoms.

In order to understand the effect of adsorbing the metal cluster on the electronic structure of the substrate, we have calculated the TDOS and PDOS for Ni 3d states for the lowest-energy configurations of $\text{Ni}_n/\text{Ga}_2\text{O}_3(100)$. As shown in Fig. 6, for the $\text{Ni}_n/\text{Ga}_2\text{O}_3$ ($n = 1, 3$ and 4) system, there is an unoccupied Ni state about 2 eV above the Fermi level. As shown in Fig. 3, the CBM of the Ga_2O_3 surface is mainly composed of Ga 4s orbitals. So the empty Ni state overlaps with the empty Ga states. Upon photoexcitation, electrons removed from the O occupied states move to the Ga unoccupied states. As the Ga unoccupied states overlap with the unoccupied Ni state, the electron can transfer from Ga to Ni. Consequently, the accumulating electrons on the Ni_n cluster may participate in proton reduction for HER. From Fig. 6, one can also find that remarkable occupied states of Ni appear in VBM of the system. During the photocatalytic reaction, an electron can be excited from an O atom to an unoccupied Ga atom. This results in the formation of a hole on the O atom. The hole can be moved from the O atom to the Ni atom in the Ni_n cluster. So in principle Ni atoms can also contribute to

the OER. However, using the Ni metal for the OER is not really appropriate because it will probably lead to NiO.

3.3. Formation of $(\text{NiO})_n$ clusters on the (100)-B surface of $\beta\text{-Ga}_2\text{O}_3$

For $(\text{NiO})_n/\text{Ga}_2\text{O}_3(100)$, the most stable energy structures obtained from our calculations are plotted in Fig. 7, and other less stable structures are shown in Fig. S2.† For every composition, key structural parameters of the lowest-energy configurations are summarized in Fig. 8. The adsorption energy for clusters is calculated based on eqn (2), and the obtained results are shown in Table 1. Negative adsorption energy means that the adsorbed structure is stable.

For the $\text{NiO}/\text{Ga}_2\text{O}_3(100)$ system, the most stable structure for this composition is obtained by introducing an additive oxygen atom to the most stable structure of $\text{Ni}/\text{Ga}_2\text{O}_3$. As shown in Fig. 8(a), the O atom binds to the surface $\text{Ga}_{5c(\text{II})}$ atom through a bond length of 1.885 Å. Due to the adsorption of the O atom, the bonded Ni atom is lifted and the bond length of $\text{Ni}-\text{O}_{3c(\text{III})}$ is lengthened by 0.18 Å compared with that of the single Ni atom adsorbed on the surface. The Ni–O bond is computed to be 1.776 Å. The adsorption energy of the NiO cluster is calculated to be -1.92 eV, indicating the stability of this configuration.

In the case of $(\text{NiO})_2/\text{Ga}_2\text{O}_3(100)$, seven structures are obtained as shown in Fig. 7 and S2.† The lowest-energy configuration consists of a $-\text{Ni}-\text{O}-\text{Ni}-\text{O}-$ four-membered ring adsorbed above the rhombic fragment of $-\text{O}-\text{Ga}-\text{O}-\text{Ga}-$ with the formation of four interfacial bonds. As can be seen from Fig. 8(b), the bond lengths of $\text{Ga}-\text{O}$, $\text{Ni}-\text{O}_{(\text{III})}$ and $\text{Ni}-\text{O}_{(\text{I})}$ are computed to be 2.000 Å, 1.940 Å and 1.935 Å, respectively. The average distance of the Ni–O bonds within the cluster is 1.886 Å, which is larger by 0.11 Å than that in the NiO monomer supported on the $\text{Ga}_2\text{O}_3(100)$ surface. The adsorption energy of this structure is predicted to be -3.67 eV, which is lower than that of NiO adsorption by 1.65 eV. Examining the relative energy of different structures from Fig. 7 and S2,† one can find that the structure with Ni_2O_2 located above Ga(I) atoms as well as between O(I) and $\text{O}_{3c(\text{III})}$ atoms is less stable than the one with Ni_2O_2 situated above the rhombic fragment of $-\text{O}-\text{Ga}-\text{O}-\text{Ga}-$.

When a $(\text{NiO})_3$ cluster was attached to the surface, both three-dimensional and two-dimensional models were considered. The most stable structure is a two-dimensional planar six-member ring structure located atop of the rhombic fragment of $-\text{O}-\text{Ga}-\text{O}-\text{Ga}-$, and with an adsorption energy of -2.57 eV. As shown in Fig. 8(c), the three Ni atoms are coordinated to surface oxygen atoms with Ni–O bonds of 2.012, 2.045 and 2.039 Å,

Table 1 The adsorption energy E_{ads} (eV), binding energy E_{nuc} (eV) and the change of the total Bader charge for Ni_n or Ni_nO_n clusters (a.u.) in $\text{Ni}_n/\text{Ga}_2\text{O}_3$ or $\text{Ni}_n\text{O}_n/\text{Ga}_2\text{O}_3$ systems, respectively. Only the most stable configuration for each composition is listed

Configuration	E_{ads}	E_{binding}	Q_{cluster}	Configuration	E_{ads}	Q_{Ni}	Q_{O}	Q_{cluster}
Ni	−2.16	−2.16	+0.58	NiO	−1.92	+0.35	−0.30	+0.05
Ni_2	−2.47	−2.20	+0.73	Ni_2O_2	−3.67	+0.45	−0.35	+0.10
Ni_3	−4.94	−2.28	+0.72	Ni_3O_3	−2.57	+1.74	−1.62	+0.12
Ni_4	−6.83	−2.34	+0.78	Ni_4O_4	−2.96	+2.18	−2.12	+0.06

Fig. 6 Density of states for the most stable configuration of (a) Ni, (b) Ni_2 , (c) Ni_3 , and (d) Ni_4 adsorbed on the $\text{Ga}_2\text{O}_3(100)$ surface. The Fermi level is shown by the vertical dashed line.

respectively. Two oxygen atoms from the cluster bind to Ga atoms from the surface and have Ga–O distances of 1.961 and 1.982 Å, respectively. The third oxygen from cluster does not connect to any Ga atom. The calculated Ni–O bond lengths in cluster are in the range of 1.797–1.910 Å.

For the Ni_4O_4 cluster adsorbed on the $\text{Ga}_2\text{O}_3(100)$ surface, several initial configurations have been optimized. For the most stable structure **a**, shown in Fig. 7 and in Fig. 8(d), the adsorbed cluster is symmetrically bonded to the surface by four Ni–O and two Ga–O bonds. Two Ni atoms bond to two O(I) with equal distances of 1.938 Å, while the other two Ni atoms bond to two O(III) with equal distances of 1.937 Å. Two oxygen atoms from the cluster form bonds with 5-fold coordinated Ga atoms from the surface, with Ga–O distances of 2.038 Å and 2.042 Å. The other two oxygen atoms from the cluster bind only internally in the cluster, and have no connection to the surface. The eight-member ring of the Ni_4O_4 cluster is made up from two kinds of Ni–O bonds with distances of 1.764 and 1.870 Å, respectively. The second most stable structure **b**, displayed in Fig. 7, shows a rectangle cluster composed of three –Ni–O– four-member rings

parallelly adsorbed on the surface, which is less stable by 0.18 eV than the lowest-energy structure. The third most stable structure **c** exhibits a cubic Ni_4O_4 cluster connected to the surface Ga and O atoms and located in the same site of the surface as the Ni_2O_2 cluster. Compared with the most stable structure, this configuration is energetically less favorable by 0.45 eV. In the gas phase, the rectangle Ni_4O_4 cluster in structure **b** is calculated to be the most stable, which is lower than the cluster in structure **a** and the cubic cluster in structure **c** by 0.04 eV and 0.87 eV, respectively. The adsorption energies computed for the Ni_4O_4 clusters on the surface are of –2.96 eV for the most stable configuration **a**, –2.74 eV for structure **b**, and –3.35 eV for structure **c**. These results suggest that the cubic Ni_4O_4 cluster adsorbs stronger on the Ga_2O_3 surface than on the planar structures.

As indicated from the calculations above, $(\text{NiO})_n$ clusters tend to maximize interfacial bonds with coordinatively unsaturated Ga and O atoms of the $\text{Ga}_2\text{O}_3(100)$ surface. The calculated adsorption energies of low-energy structures indicate that there are strong interactions between nickel

Fig. 7 Stable configurations of $\text{Ni}_n\text{O}_n/\text{Ga}_2\text{O}_3(100)$ ($n = 1-4$) clusters (side and top views). Relative energies with respect to the corresponding lowest-energy structure are shown. Coloring scheme: red (surface O), brown (Ga), yellow (adsorbed O) and blue (Ni). The same color scheme applies to all the following figures.

Fig. 8 Geometrical parameters for the most stable structures of Ni_nO_n/Ga₂O₃(100) ($n = 1-4$): (a) Ni, (b) Ni₂, (c) Ni₃, and (d) Ni₄.

oxide nanoclusters and the surface. Unlike Ni_n clusters, (NiO)_n clusters prefer to be formed above the rhombic fragment composed of Ga_{5c(III)}, O₁ and O_{3c(III)} atoms. In other

words, small Ni_n and (NiO)_n clusters will tend to form on different sites of the surface.

The charge distribution at the interface between the (NiO)_n clusters and the surface has been examined through the use of the Bader charge analysis. As shown in Table 1, after attaching to the surface, the Ni atoms from the (NiO)_n clusters show positive charge while the O negative charge. This indicates that the charge flow occurs from Ni atoms to surface O atoms, and from surface Ga atoms to cluster O atoms simultaneously. The number of electrons received by O in (NiO)_n clusters is slightly smaller than the number of electrons given away by Ni. As a result, the total charge on the (NiO)_n cluster is slightly positive. With the increase of the cluster size, the amount of the charge transferred between the surface and the cluster increases significantly due to the larger number of bonds formed between the surface and the cluster.

More insight into the adsorption effects of the (NiO)_n clusters can be obtained from the analysis of the electronic density of states. In Fig. 9 we present the calculated HSE06 TDOS and PDOS for Ni 3d states and O 2p states for every (NiO)_n cluster in the most stable adsorbed configuration. The strong mixing of O and Ni states is indicative of the covalent bonding in NiO. Some of mixed states are located in VBM and others are at and below

Fig. 9 Density of states for the most stable configuration of (a) NiO, (b) Ni₂O₂, (c) Ni₃O₃ and (d) Ni₄O₄ adsorbed on the Ga₂O₃(100) surface. The Fermi level is shown by the vertical dashed line.

the Fermi level. Upon light irradiation, the electrons in the VBM of Ga_2O_3 are excited to the CBM, while the holes are left in the VBM. Since the occupied states from the $(\text{NiO})_n$ cluster are higher in energy than the VBM, the electrons in $(\text{NiO})_n$ tend to transfer to the VBM of Ga_2O_3 . And then the holes generated in $(\text{NiO})_n$ clusters will participate in the photocatalytic OER. As shown in Fig. 9, one can find that some Ni unoccupied states are located ~ 4.5 eV above the Fermi level. The high position of the Ni unoccupied states will make the HER unfavorable.

4. Conclusions

In this work, we have performed a systematic DFT study on the relative stabilities of the low-index surfaces of $\beta\text{-Ga}_2\text{O}_3$, and on the stable adsorption sites for Ni_n and $(\text{NiO})_n$ clusters supported on the surface. It was found that small Ni_n clusters tend to be formed above Ga(I) atoms and between O(I) and $\text{O}_{3c}(\text{III})$ atoms, while $(\text{NiO})_n$ clusters tend to grow on the rhombic fragment composed of $\text{Ga}_{5c}(\text{III})$, O(I) and $\text{O}_{3c}(\text{III})$ atoms. For $\text{Ni}_n/\text{Ga}_2\text{O}_3$ systems, the binding energy decreases with the increment of Ni coverage (from Ni_1 to Ni_4), which indicates that larger clusters are energetically more stable than smaller ones. $(\text{NiO})_n$ clusters are found to strongly adsorb on the Ga_2O_3 surface due to the negative adsorption energies within -1.9 eV to -3.7 eV.

The electronic structure analyses indicate that for $\text{Ni}_n/\text{Ga}_2\text{O}_3$ systems, the unoccupied Ni states overlap with the Ga unoccupied states. Upon the irradiation of light, the excited electron can transfer from Ga to Ni. Consequently, the accumulating electrons on Ni_n clusters may participate in the photocatalytic HER. As to $(\text{NiO})_n/\text{Ga}_2\text{O}_3$, occupied states from the $(\text{NiO})_n$ cluster may accept the holes from O atoms in the Ga_2O_3 surface to take part in the photocatalytic OER. The determination of the stable structures and electronic structures for Ni_n and $(\text{NiO})_n$ adsorbed on the $\beta\text{-Ga}_2\text{O}_3$ surface provides a foundation for further investigations on the mechanism of the photocatalytic water-splitting reaction in the $\text{NiO}_x/\text{Ga}_2\text{O}_3$ system as well as other $\text{NiO}_x/\text{semiconductor}$ systems.

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