Conditions for magnetic and electronic properties of ultrathin Ni–Fe hydroxide nanosheets as catalysts: a DFT+*U* study

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ABSTRACT The effects of cation ordering and surface compensating anions on the magnetic structure and catalytic properties of unilamellar Ni–Fe hydroxide nanosheets are studied by using the density functional theory (DFT) plus *U* method. Fe-segregation in the nanosheets yields magnetic domains with different spin alignments, while the surface compensating anions affect the local moments and valence states of the Fe atoms. The two conditions do not radically change the super-exchange nature of interactions between the paramagnetic metal centers, but facilitate the formation of various magnetic superlattices in the nanosheets. The calculated free energy change of the intermediates shows that the most stable magnetic structure of Ni–Fe hydroxide nanosheets exhibits superior catalytic activity towards oxygen reduction/evolution reactions, which is indicative of magnetic catalyst. This is due to the cycle transition between Fe²⁺ and Fe³⁺ ions in the reactions, which determines the sequence of cleavage of the O–H bond and the release of the OH group, controlling the rate-limiting steps of the reaction. The relationship of magnetism and catalytic activity of Ni–Fe hydroxide nanosheets is established by the valence state change of the Fe ions, which will be helpful to open the way for the design of hydroxide/layered double hydroxides (LDHs)-based magnetic catalysts.

Keywords: condition effects, DFT+*U*, Ni–Fe hydroxide nanosheets, magnetic catalyst, electron magnetism-electron catalysis

INTRODUCTION

In the last decade, a large number of two-dimensional (2D) materials have been fabricated by the top-down and bottom-up approaches [1,2], and have attracted much attention [3,4]. Among the available candidates, the layered double hydroxides (LDHs) are frequently in the form of bulk-like crystal [5], by the electrostatic attraction between

charge compensating anions and positively charged hydroxide layers [6]. To extract the unilamellar sheet from bulk crystal, an exfoliation by soni-mechanical treatment has been developed earlier [7]; only very recently, a direct synthesis by the solution-phase nucleation was reported [8], making the preparation easier and more convenient. In principle, the nanosheets have ultimate 2D anisotropy and positive charge, thus allowing for peculiar properties and diverse potential applications. Besides being used as an electrode catalyst for fuel cells [9,10] and an efficient carrier for gene delivery [11], these metal hydroxide nanosheets after delamination are also considered as the building blocks of novel nanocomposites [12,13], in which the intrinsic properties of hydroxide layers dexterously combine with the derived nature from intercalated anionic organic/inorganic moieties, for highly efficient supercapacitors [14,15].

Previous studies of ultrathin 2D metal films have largely appeared on the use of photoelectric devices [16,17]. By contrast, the efforts devoted to describing the magneto-electronics are very scarce [18]. The reason is probably that the preparations of ultrathin freestanding pristine 2D transition metal and metal oxide films are very difficult, due to 3D non-directional metallic or directional covalent bonding [19]. The unilamellar transition metal hydroxide nanosheet is a natural freestanding layer without surface dangling bonds, which endows its irreplaceable advantage in the magnetic study. Cheap Ni–Fe LDHs not only possess exciting catalytic properties which make them be used as catalysts for oxidation reactions [9,20–22], but also can be exfoliated to form the unilamellar nanosheet, exhibiting 2D intrinsic magnetization [23]. In particular, a recent experiment revealed that the magnetic interaction be-

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tween metal centers in Ni-Fe LDHs significantly enhances the electrocatalytic performance of oxygen evolution reaction (OER) in alkaline media [24]. This is a strong indication of the relationship between electrocatalytic activity and magnetic properties of the catalyst, also offering a new strategy for developing catalytic activity of LDHs, that is, by the magnetic field. Few studies on electron magnetism-electron catalysis (not to mention magnetic catalysis of hydroxide nanosheets) have been done so far. So, it is very necessary to clarify the origin and nature of the magnetism-related catalytic properties of unilamellar Ni-Fe hydroxide nanosheets, either as the basic building blocks for nanocomposites or as a model for 2D magnetic systems.

In this article, we theoretically studied the magnetic coupling behaviors in the ordered/disordered arrangement of metal ions and magnetic structure of Ni-Fe hydroxide nanosheets. Crucially, we compared the electrocatalytic performances of these Ni-Fe hydroxide nanosheets with different magnetic structures in oxygen reduction/evolution reactions (ORR/OER), by the free energy change of the intermediates. Furthermore, we discussed the relationship between intralayer magnetic coupling and the change of valence states of Fe ions, which was to some extent associated with the mechanism of catalytic reactions involving magnetic Ni-Fe LDHs.

CALCULATION MODELS AND METHOD

From the fundamental scientific point of view, we chose unilamellar Ni₂Fe hydroxide nanosheets, in which all metal ions are paramagnetic, as prototypes. In the periodic slab models, the $p(2\sqrt{3} \times 2\sqrt{3})$ rhombohedral supercell (Figs 1a and 2a) was adopted to study the magnetic ordering and magnetic properties of the ordered/disordered Ni₂Fe hydroxide nanosheets, and the effects of surface compensating anions on the magnetism and the valence states of metal ions. The Cl atoms were introduced to keep system electrically neutral for the LDH model. The separation between adjacent slabs was 15 Å, which was much larger than the van der Waals thickness of the brucite sheets (~

4.7 Å). All spin-polarized density functional theory (DFT) calculations were carried out using the Vienna *ab initio* simulation package (VASP) [25]. The PBE-GGA [26] and the PAW method [27] with the cut-off energy of 400 eV were used. Following previous theoretical studies of LDHs [21,28], the U parameters of DFT + U approximation were chosen to be 4.0 and 3.0 eV for Ni and Fe, respectively. The integration over the Brillouin zone was done by using the Monkhorst-Pack scheme with a $3 \times 3 \times 1$ mesh for all calculations. Complete optimization was performed until the force on each ion was less than 0.02 eV Å⁻¹. Bader charge analysis, valence bond simulation [29] and atomic magnetic moment on each ion were employed to unveil the oxidation states of the Fe ions of nanosheets.

RESULTS AND DISCUSSION

It is of importance to guarantee the ordered arrangement of constituent atoms in an ideal 2D material for charge transport applications [30]. The one specific to LDHs is that the cation arrangement remains highly ordered in the layers. Our results show that for the unilamellar Ni₂Fe hydroxide nanosheet, the ordered arrangement of cations (Fig. 1a) is more energetically favorable than the disordered one, where the position of a Ni-Fe pair is swapped to construct a local Fe-segregated region (Fe₂-Fe₃-Fe₄ in Fig. 2a). This totally follows the rule of the Coulomb repulsion between two Fe ions that occupy the neighboring octahedra interstitial sites [19]. But the calculated ordering energy of 0.151 eV/supercell is only 1/3 of that of Mg₂Al LDHs (0.456 eV/supercell) [31]. In essence, such energy difference may owe to different natures of d-electrons of transition metals (Ni, Fe) and sp-electrons of simple metals (Mg, Al). Not surprisingly, the intriguing characteristics make Ni₂Fe hydroxide nanosheets be possible to form desired super-lattices. This on the one hand insures the unity of the performance, on the other hand means that the random arrangement of cations could be probably occurred in not very harsh conditions.

Therefore, we need to pay attention to the effects of

Figure 1 (a) Structure and (b) spin density distributions of unilamellar ordered Ni₂Fe hydroxide nanosheets. In (a), the black dashed box indicates the $p(2\sqrt{3} \times 2\sqrt{3})$ rhombohedral supercell. There contains three magnetic sublattices composed of Ni₁, Ni₂ and Fe. The inset shows the hydroxyl environment, Ni₂Fe-OH (highlighted by the red circle). The black and red arrows indicate the spin-up and spin-down electron motion, respectively. In (b), yellow and glaucous iso-surfaces correspond to the spin-up and spin-down regions, respectively (the iso-value is 0.05 a.u.). (c) The subnetwork with the AFM alignment of the Ni and Fe ions. The blue, purple, red, white and green balls represent the Ni, Fe, O, H and Cl atoms, respectively.

Figure 2 (a) Structure and (b) spin density distributions of unilamellar disordered Ni_2Fe hydroxide nanosheets induced by Fe-segregation. In (a), three major types of hydroxyl local environments: $\text{Ni}_3\text{-OH}$ (green circle), $\text{Ni}_2\text{Fe-OH}$ (red circle), and $\text{NiFe}_2\text{-OH}$ (orange circle) are shown in the sets. The black and red arrows indicate the spin-up and spin-down electron motion, respectively. In (b), yellow and glaucous isosurfaces correspond to the spin-up and spin-down regions, respectively (the iso-value is 0.05 a.u.). (c) The destroying magnetic super-lattice composed of the Ni and Fe ions. The blue, purple, red, white and green balls represent the Ni, Fe, O, H and Cl atoms, respectively.

cation-ordering/disordering on the magnetic properties of unilamellar Ni_2Fe hydroxide nanosheets. There is only one hydroxyl environment, which is defined by the coordinated metal ions (i.e., $\text{Ni}_2\text{Fe-OH}$ in the inset of Fig. 1a), in the ordered sheet [31]. We consider three magnetic sublattices following the sequence of the three paramagnetic cations (Ni_1 , Ni_2 and Fe) in the unit cell (Fig. 1a). The corresponding magnetic configurations are illustrated as follows: $(++ +)$, $(++ -)$, and $(+ - +)$. The $+$ and $-$ designate the spin-up and spin-down electron motion, respectively. The total energies and magnetic moments of the three configurations are listed in Table 1. We can see that the $(++ -)$ configuration is the energetically lowest. In particular, it is also lower than the other $(+ - +)$ configuration by about 133 meV/supercell. Whereas the highest total energy is possessed by the $(+++)$ configuration which lies 229 meV/supercell above the ground state.

As expected, the magnetism of Ni_2Fe hydroxide nanosheets arises from the coupling between paramagnetic Ni and Fe ions. Interestingly, the local moments of the Ni and Fe are quite stable in the three magnetic configurations, which are respectively close to the experimental value of 1.6–1.8 μ_B for NiO [32] and somewhat smaller than that of 4.6–4.9 μ_B for Fe_2O_3 [33]. These results are compatible with the view that the valence states of the Ni and Fe ions in Ni_2Fe hydroxides and respective metal oxides are identical to a certain extent, indicative of similar coordination environments. Note that the calculated moments of the H and Cl are zero. Similarly, the local

moment of the O in the ground state is also very small, only 0.04 μ_B . Even so, the magnetic coupling between metal ions is still occurring *via* the linked O–H. Typically, the Ni-O(H)-Fe and Ni-O(H)-Ni interactions exhibit the antiferromagnetic (AFM) and ferromagnetic (FM) couplings, respectively (Fig. 1b). As a consequence, the intralayer AFM interactions between Ni and Fe atoms yield a total moment of 3.7 μ_B per supercell, generating collective magnetism in the ordered nanosheet by the long-range magnetic coupling [34]. The present results agree well with the previous measurement on spontaneous magnetization of Ni–Fe LDHs [23]. That is, the magnetic exchange in unilamellar Ni_2Fe hydroxide nanosheets is dominated by the AFM alignment of the non-compensating Ni^{2+} and Fe^{3+} subnetworks, with the atomic spins aligned parallel to each other in each subnetwork (Fig. 1c). It behaves as an isotropic magnetic super-lattice.

On the other hand, the calculated ordering energy (151 meV) is almost equal to the magnetic transition energy (133 meV) between $(++ -)$ and $(+ - +)$ configurations in the ordered Ni_2Fe hydroxide nanosheets. We reasonably believe that for such transition metal hydroxide nanosheets, the magnetic property might have an anomalous relationship with the ordering of cation arrangement under realistic conditions. In the disordered Ni_2Fe ones, there are three major types of hydroxyl local environments: $\text{Ni}_3\text{-OH}$, $\text{Ni}_2\text{Fe-OH}$ and $\text{NiFe}_2\text{-OH}$ (the insets of Fig. 2a) [31]. Based on the above calculations and analyses on the ordered ones, in combination with the experimental obser-

Table 1 The total energy E_{tot} (meV per supercell) (measured from the $(++ -)$ state), local moments of the Ni, Fe and O atoms (μ_B), and total moment of domain (μ_B per supercell) for different magnetic configurations of unilamellar ordered Ni_2Fe hydroxide nanosheets

Configuration	E_{tot}	Moment			
		Ni	Fe	O	Domain
$(++ -)$	0	1.70	−4.22	0.04	−3.70
$(+ - +)$	133	±1.74	4.23	0.12	19.40
$(+++)$	229	1.73	4.24	0.21	35.11

vations [23], we still assigned the Ni–O(H)–Ni coupling to be FM and the Ni–O(H)–Fe coupling to be AFM. In this case, the calculation models will be integrated and simplified, that is, there are three magnetic sublattices to be considered in the disordered one. According to the sequence of the paramagnetic cations (Ni, Fe_{1–3} and Fe₄) in the unit cell (Fig. 2a), the magnetic configurations are illustrated as follows: (+ + +), (+ – –), and (+ – +). From Table 2, we can see that the (+ – +) configuration is the energetically lowest, followed by the (+ – –), and finally the (+ + +) one. The ground state shows that the Fe₂(Fe₃)–O(H)–Fe₄ coupling is AFM, but the energy difference between AFM and FM coupling of Fe₂(Fe₃)–O(H)–Fe₄ is only 13 meV per supercell, indicating that the two magnetic configurations are nearly degenerate. At this rate, we can confirm that the charge repulsion, beyond the magnetic coupling, of M³⁺–O–M³⁺ linkages dominates the ordering of LDHs, which coincides with the previous view [35]. The random arrangement of Fe–O–Fe pairs certainly will disrupt the well-ordered magnetic network, generating spin frustration. This also validates the experimental prediction, in which the precise analysis of the magnetic data is somewhat difficult [23]. Importantly, Table 2 shows that the local moments of the Ni and Fe remain unchanged. This again corroborates that the valence states of the Ni and Fe atoms in Ni₂Fe hydroxides (whether ordered or disordered) remain +2 and +3. Likewise, a periodic anisotropic magnetic super-lattice with a moment of 6 μ_B per supercell would likely be achieved (Fig. 2b, c). Overall, collective magnetism is spontaneous for either ordered or disordered Ni₂Fe hydroxide nanosheets in the ground state, which is consistent with the experimental results of Ni–Fe LDHs [23]. Simultaneously, the observed difference of magnetic property guides that we can distinguish the long-range or short-range order in Ni₂Fe hydroxide nanosheets by the nanoscale magnetic probe.

In addition to this, recently, another attractive application of transition metal LDHs is as an excellent electrode catalyst of fuel cells [9,10,22,36]. Here the ORR/OER is employed as the probe reaction to assess the relationship between electron magnetism and electron catalysis of Ni–Fe hydroxide nanosheets. For comparison conve-

niently, we only took into account three kinds of representative magnetic structures of the ordered Ni₂Fe hydroxide nanosheets: the most stable (+ + –) configuration, the most unstable (+ + +) configuration and the non-magnetic (NM) configuration, respectively. A series of calculations on the thermodynamic free energy change of the intermediates of ORR/OER in alkaline media were performed within the framework of the DFT. The OER/ORR is a multi-electron reaction, which is recognized to include four elementary reaction steps involving three intermediates that are OH*, O* and OOH*. In alkaline medium, the OER proceeds through the formation of OH* from OH[–] of alkaline solution, followed by the oxidation of OH* to O* and H₂O, and the reaction of O* with OH[–] again to form OOH*, finally the desorption of H⁺ from OOH* to produce O₂ [37]. While the ORR proceeds in the reverse direction [38,39]. Fig. 3 is the calculated free energy diagram at the equilibrium potential ($U_{RHE}^0 = 1.23$ V) in the overall ORR/OER pathway of Ni–Fe hydroxide nanosheets in alkaline media. Our results show that the (+ + –) configuration has the most ideal thermodynamic free energy change of the intermediates, that is, $|\Delta G_{OOH^*}|$, $|\Delta G_{O^*}|$ and $|\Delta G_{OH^*}|$ are 0.91, 0.19, 0.21 eV, which are somewhat close to 0. This indicates little energy would be wasted to activate the ORR/OER processes [37,38]. It is a good bi-functional electrocatalyst for OER [22] and ORR.

While for the (+ + +) configuration, $|\Delta G_{O^*}|$ and $|\Delta G_{OH^*}|$ are so large as to exceed 1.25 eV, even though $|\Delta G_{OOH^*}|$ (0.86 eV) is somewhat smaller than that of the (+ + –) configuration. The reaction from O* to OOH* for the OER or the first electron transfer step to reduce the O₂* to OOH* for the ORR is endothermic, which is the respective rate-limiting step and significantly inhibits the ORR/OER. Meanwhile, although the $|\Delta G_{O^*}|$ and $|\Delta G_{OH^*}|$ are negative, too large values mean that the chemical adsorption of O* and OH* is too strong, which is also unfavorable for the subsequent electrocatalytic reactions. Very important information obtained from our study is that if the magnetic coupling effects between paramagnetic metal cations (i.e., the non-magnetic configuration) were ignored, the ORR/OER is hardly occurred under normal conditions due to too

Table 2 The total energy E_{tot} (meV per supercell) (measured from the (+ – +) state), local moments of the Ni, Fe₄ and O (μ_B), and total moment of domain (μ_B per supercell) for different magnetic configurations of unilamellar disordered Ni₂Fe hydroxide nanosheets

Configuration	E_{tot}	Moment			
		Ni	Fe	O	Domain
(+ – +)	0	1.71	4.21	0.12	–5.99
(+ – –)	13	1.70	–4.22	0.04	–3.71
(+ + +)	232	1.73	4.24	0.21	35.10

Figure 3 The calculated ORR/OER free energy diagram at the equilibrium potential on different magnetic structures of unilamellar ordered Ni_2Fe hydroxide nanosheets, with respect to the non-magnetic state. The most stable (+ + -) configuration, the NM configuration and the most unstable (+ + +) configuration are depicted by the blue, Magenta and green lines, respectively. The atomic structure of every elementary step in the ORR/OER is shown in the upper inset.

large $|\Delta G_{\text{OOH}^*}|$ (2.20 eV), even though the $|\Delta G_{\text{O}^*}|$ (0.62 eV) and $|\Delta G_{\text{OH}^*}|$ (0.29 eV) are close to 0, like as the (+ + -) configuration. In particular, for the ORR, a large $|\Delta G_{\text{O}_2^*}|$ (1.53 eV) also indicates that the first electron transfer step to reduce the adsorbed O_2 to OOH^* is endothermic, requiring an excess energy of 3.73 eV. Similarly, for the OER, the endothermic reaction from O^* to OOH^* needs an excess energy of 2.81 eV, too. Overall, the above comparison intuitively reflects the spontaneous magnetism is a crucially decisive factor for the enhanced electrocatalytic performance of OER/ORR of Ni-Fe LDHs in alkaline media. The present result is not only consistent with the experimental observation [24] but also highlights the concept of magnetic catalysis, that is, only the regulation magnetic coupling is compatible with magnetic catalyst.

It was proposed that the Fe atoms, rather than the Ni atoms, are the available sites for reactions in Ni-Fe LDHs [21]. This might be associated with the valence state change of the Fe atom in the reaction. To understand the magneto-catalysis behaviors of LDHs, we conducted

the study on the change of valence states of paramagnetic atoms (Fe and Ni). In detail, surface compensating anions were removed because the adhesion energy of the Cl atom on the sheet (2.70 eV) was weaker than the dissociation energies of O-H (5.29 eV per H atom) or Fe(Ni)-OH bonds (3.02 eV per OH group), and a new double metal hydroxide (hereafter referred to as $\text{Ni}_2\text{Fe}(\text{OH})_6$) was achieved in thermodynamics. As a calibration reference, in unilamellar Ni_2Fe hydroxide nanosheets, Bader charge analysis shows that 1.512 e are transferred from the Fe atom to the OH groups, and correspondingly, the valence bond simulation reveals that the average value of valence state for the Fe ion is 2.946, which is nearly equal to the theoretical valence of FeOOH (2.925) [21], as expected for Fe^{3+} . Relatively, there are smaller electron transfers (1.480 e) from the Fe to the OH in $\text{Ni}_2\text{Fe}(\text{OH})_6$. The calculated average valence of the Fe is 2.232, which is more close to the theoretical valence of FeO (1.952) [21]. Both of them evidence that the Fe in $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets is indeed reduced from the valence state of +3 to +2. Like the case of the ordered Ni_2Fe hydroxide nanosheets (the sequence of Ni_1 , Ni_2 and Fe), there are three magnetic configurations in the $\text{Ni}_2\text{Fe}(\text{OH})_6$ unit cell as follows: (+ + +), (+ + -), and (+ - +). But the total energy shows that the (+ + -) and (+ - +) configurations are nearly degenerate (Table 3). Even for the (+ + +) configuration, there is only 118 meV per supercell higher than the ground state. These results differ from those of the ordered Ni_2Fe hydroxide nanosheets, an indication of the particularity of Fe^{2+} with respect to Fe^{3+} . That is, the doping of Fe^{2+} may not change the magnetic structure of $\text{Ni}(\text{OH})_2$ nanosheets, which exhibits the AFM coupling between Ni^{2+} ions through the OH group [40]. The magnetism analysis further shows that the moment of the Ni^{2+} ion remains quite stable, $1.71 \mu_{\text{B}}$, while the moment of the Fe^{2+} ion is dramatically reduced to be $3.71 \mu_{\text{B}}$, which is close to that of FeO ($3.46 \mu_{\text{B}}$ for DFT calculations and $4.2 \mu_{\text{B}}$ for experiments) [41,42]. Interestingly, the two stable (+ + -) and (+ - +) configurations have 0.02 and $3.90 \mu_{\text{B}}$ per unit cell, respectively. The former seems a typical AFM semiconductor, in which the spin effect of one Fe^{2+} ion

Table 3 The total energy E_{tot} (meV per supercell) (with respect to the (+ + -) state), local moments of the Ni, Fe and O (μ_{B}), and total moment of domain (supercell) (μ_{B}) for different magnetic configurations of $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets

Configuration	E_{tot}	Moment			
		Ni	Fe	O	Domain
(+ + -)	0	1.71	-3.71	0.05	0.06
(+ - +)	5	± 1.72	3.71	0.03	15.59
(+ + +)	118	1.72	3.71	0.11	31.25

Figure 4 The spin density distributions of $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets of (a) $(+ + -)$ and (b) $(+ - +)$ configurations, respectively, forming different magnetic subnetworks, as describe in (c) antiferromagnetic and (d) ferromagnetic semiconductors. Yellow and glaucous isosurfaces correspond to spin-up and spin-down electron motion, respectively (the isovalue is 0.05 a.u.). The blue, purple, red and white balls represent the Ni, Fe, O and H atoms, respectively.

counteracts those of two Ni^{2+} ions; while the latter is a typical paramagnet (Fig. 4). Following the viewpoint of Néel [43], in practice, for the AFM $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheet, there possibly exhibits super-paramagnetic or spin glass behavior, even weak ferromagnetism with a permanent magnetic moments, due to size confinement effects. It is expected that the attention of $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets will be increased by virtue of their potential for exhibiting magnetization reversal by quantum tunneling, like the famous AFM nanoparticles.

In the studies of common chemical reactions, Nørskov *et al.* [44,45] also developed a trends-based volcano analysis to estimate the performance of catalysts using the adsorption strengths of intermediates on the active sites. Our calculations show that the decomposition energies of the H atom from the Ni_2Fe and $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets are -5.29 and -3.61 eV, while those of the OH group are -3.02 and -4.54 eV, respectively. These present results mean that in Ni_2Fe hydroxide nanosheets, the OH group rather than the H atom as a whole to participate in the reaction because the OH–Fe bond breaking process is more easily accomplished than the OH bond; while in $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets, the situation is different, i.e., the H works as a more general reaction intermediate than the OH, owing to the distinctly opposite trend of the breaking of OH–Fe and OH bonds. This is compatible with the valence states of the Fe ions in the two materials. The present results propose that as the same magnetic catalysts, Ni_2Fe hydroxide and $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets have different contributions to chemical reactions, and promote different reaction pathways, showing the catalytic diversity of hydroxide nanosheets.

In essence, the Fe^{3+} and Fe^{2+} ions in the magnetic LDHs correspond to different occupied conditions of 3d electrons, mixing with the e_1 magnetic orbitals of the Ni^{2+} ions. Therefore, it is by the bridge of valence states that we can combine the magnetic coupling between metal ions with the catalytic activity of Ni–Fe hydroxide nanosheets. A more comprehensive understanding of the magnetism-related catalytic properties of unilamellar Ni–Fe hydroxide nanosheets can be obtained from the density of states (DOS) and band structures, as shown in Fig. 5. We can see that the two nanosheets are 2D paramagnetic or ferromagnetic semiconductors, and the basic frameworks are maintained by the hybridization of O 2p orbitals and Ni(Fe) 3d orbitals. More precisely, the band gaps of Ni_2Fe hydroxide are about 0.45 and 0.30 eV for the spin-up and spin-down channels, in which the valence band maximum (VBM) is only contributed from the Ni 3d states, while the conduction band minimum (CBM) is composed of the Ni 3d states and anti-parallel Fe 3d states. Furthermore, Table 4 gives the d-orbital occupations of the Ni and Fe ions in the ordered Ni_2Fe hydroxide nanosheet. As expected, the distinctly opposite d-orbital occupations of the spin-up and spin-down levels also indicate that it is the AFM coupling between the Ni and Fe sites, which is to a certain extent compatible with their local moments shown in Table 1. The small contributions of the O atoms in the CBM and VBM will further strengthen the view that the magnetic ordering of the Ni_2Fe hydroxide nanosheet results from the super-exchange interaction between Ni and Fe ions *via* the OH group. By contrast, the spin-polarized effects are relatively obvious in $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets. In particular, there are impurity bands just below the Fermi level in the gap of 1.45 eV for the spin-down channel, while the gap for the spin-up channel is also increased to 1.20 eV. As expected, the occupied impurity states are contributed from the Fe 3d, clearly indicative of the reduction of Fe^{3+} to Fe^{2+} due to the electron withdrawing characteristics. This again evidences that the Fe^{3+} ions rather than the Ni^{2+} ions in the LDHs are indeed the active sites, which agrees with the theoretical prediction based on the experiment [21]. And such, the impurity states, contributing to the magnetic coercivity for the nanosheet, instead of the VBM certainly will make a dominant effect on the successive oxidation-reduction reaction; and from another point of view, this verifies the fact that the real Ni_2Fe LDHs are in general stable [23,24,31]. Crucially, the calculated adhesion energy of one Cl atom on the Ni_2Fe hydroxide nanosheet is -2.70 eV, which is weaker than the dissociation energies of O–H (-5.29 eV per H atom) and Fe(Ni)–OH bonds (-3.02 eV

Figure 5 Total and projected DOS and band structures of (a) Ni_2Fe hydroxide, and (b) $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets in the ground state, respectively. The Fermi level is set at zero. For the sake of brevity, the projected DOS of the Cl species are excluded in (a).

Table 4 Populations of the d orbitals of the Ni and Fe in the ordered Ni_2Fe hydroxide nanosheet (in Units of e^{a})

Orbitals	Ni			Fe		
	e_1	e_2	a_1	e_1	e_2	a_1
Spin-up	1.46(2)	1.08(2)	0.96(1)	2(2)	2(2)	0.97(1)
Spin-down	2(2)	2(2)	0.97(1)	0.36(0)	0.42 (2)	0.08(1)

a) For comparison, the corresponding values of isolated Ni and Fe atoms in a crystal field are displayed in the parentheses.

per OH group). At elevated temperature during the thermal decomposition, the Cl species certainly will first remove from the strict nanosheet, rather than $-\text{OH}$ or $-\text{H}$. This ensures the $\text{Ni}_2\text{Fe}(\text{OH})_6$ nanosheets can be achieved in thermodynamics, even be metastable at an intermediate temperature before the formation of mixed metal oxides. In addition, since the $\text{Ni}(\text{OH})_2$ and $\text{Fe}(\text{OH})_2$ are the brucite

structure, we believe that brucite-like $\text{Ni}_2\text{Fe}(\text{OH})_6$ can also be formed by the substitution of Fe for Ni in the $\text{Ni}(\text{OH})_2$ or the co-precipitation of Fe^{2+} with $\text{Ni}(\text{OH})_2$ in a reductive environment.

CONCLUSIONS

On the basic of spin-polarized DFT + U calculations,

we studied the diversity and stability of magnetic structure of unilamellar Ni_2Fe hydroxide nanosheets under practical conditions. In the Ni-Fe LDHs, Fe-segregation does not change the AFM coupling between Ni and Fe ions, but allows for the energy-degenerated magnetic domains with different spin alignments. This information would likely guide new magnetic probe measurement for the long-range/short-range order and the assembly of magnetic superlattices in Ni_2Fe hydroxide nanosheets. Furthermore, as surface compensating anions are excluded, the Fe ions are reduced from +3 to +2 in the hydroxide nanosheets, but the super-exchange nature of the 2D paramagnetic or ferrimagnetic semiconductor is retained. The induced impurity states in the gap not only lead to the spin splitting of 3d electrons, but also affect the catalytic activity by promoting the cleavage of the O-H bond. The calculated free energy change of the intermediates in the ORR/OER demonstrates superior catalytic activity of Ni-Fe hydroxide nanosheets with the most stable magnetic structure. It indicates that as an available magnetic catalyst, the coupling between paramagnetic metal atoms certainly will affect the valence state change of active metal atoms, thus facilitating the chemical reactions.

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- Novoselov KS, Geim AK, Morozov SV, *et al.* Electric field effect in atomically thin carbon films. *Science*, 2004, 306: 666–669
- Coleman JN, Lotya M, O'Neill A, *et al.* Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science*, 2011, 331: 568–571
- Geim AK, Novoselov KS. The rise of graphene. *Nat Mater*, 2007, 6: 183–191
- Chhowalla M, Shin HS, Eda G, *et al.* The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat Chem*, 2013, 5: 263–275
- Evans DG, Slade RCT. Structural aspects of layered double hydroxides. Layered Double Hydroxides. Berlin: Springer Berlin Heidelberg, 2006
- Fan G, Li F, Evans DG, *et al.* Catalytic applications of layered double hydroxides: recent advances and perspectives. *Chem Soc Rev*, 2014, 43: 7040–7066
- Li L, Ma R, Ebina Y, *et al.* Positively charged nanosheets derived via total delamination of layered double hydroxides. *Chem Mater*, 2005, 17: 4386–4391
- Liang D, Yue W, Sun G, *et al.* Direct synthesis of unilamellar MgAl -LDH nanosheets and stacking in aqueous solution. *Langmuir*, 2015, 31: 12464–12471
- Gong M, Dai H. A mini review of NiFe-based materials as highly active oxygen evolution reaction electrocatalysts. *Nano Res*, 2015, 8: 23–39
- Gong M, Wang DY, Chen CC, *et al.* A mini review on nickel-based electrocatalysts for alkaline hydrogen evolution reaction. *Nano Res*, 2016, 9: 28–46
- Li L, Gu W, Liu J, *et al.* Amine-functionalized SiO_2 nanodot-coated layered double hydroxide nanocomposites for enhanced gene delivery. *Nano Res*, 2015, 8: 682–694
- Wang Q, O'Hare D. Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets. *Chem Rev*, 2012, 112: 4124–4155
- Wang Z, Jia W, Jiang M, *et al.* Microwave-assisted synthesis of layer-by-layer ultra-large and thin NiAl -LDH/RGO nanocomposites and their excellent performance as electrodes. *Sci China Mater*, 2015, 58: 944–952
- Mahmood N, Tahir M, Mahmood A, *et al.* Role of anions on structure and pseudocapacitive performance of metal double hydroxides decorated with nitrogen-doped graphene. *Sci China Mater*, 2015, 58: 114–125
- Yang M, Cheng H, Gu Y, *et al.* Facile electrodeposition of 3D concentration-gradient Ni-Co hydroxide nanostructures on nickel foam as high performance electrodes for asymmetric supercapacitors. *Nano Res*, 2015, 8: 2744–2754
- Rakic AD, Djurisic AB, Elazar JM, *et al.* Optical properties of metallic films for vertical-cavity optoelectronic devices. *Appl Opt*, 1998, 37: 5271–5283
- Atwater HA, Polman A. Plasmonics for improved photovoltaic devices. *Nat Mater*, 2010, 9: 205–213
- Prinz GA. Magneto-electronics. *Science*, 1998, 282: 1660–1663
- Pauling L. The Nature of the Chemical Bond and the Structure of Molecules and Crystals: an Introduction to Modern Structural Chemistry (3rd ed.). New York: Cornell University Press, 1960
- Luo J, Im JH, Mayer MT, *et al.* Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts. *Science*, 2014, 345: 1593–1596
- Chen G, Zhao Y, Fu G, *et al.* Interfacial effects in iron-nickel hydroxide-platinum nanoparticles enhance catalytic oxidation. *Science*, 2014, 344: 495–499
- Friebel D, Louie MW, Bajdich M, *et al.* Identification of highly active Fe sites in $(\text{Ni,Fe})\text{OOH}$ for electrocatalytic water splitting. *J Am Chem Soc*, 2015, 137: 1305–1313
- Coronado E, Galán-Mascarós JR, Martí-Gastaldo C, *et al.* Spontaneous magnetization in Ni-Al and Ni-Fe layered double hydroxides. *Inorg Chem*, 2008, 47: 9103–9110
- Oliver-Tolentino MA, Vázquez-Samperio J, Manzo-Robledo A, *et al.* An approach to understanding the electrocatalytic activity enhancement by superexchange interaction toward OER in alkaline media of Ni-Fe LDH. *J Phys Chem C*, 2014, 118: 22432–22438
- Kresse G, Furthmüller J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys Rev B*, 1996, 54: 11169–11186
- Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett*, 1996, 77: 3865–3868
- Blöchl PE. Projector augmented-wave method. *Phys Rev B*, 1994, 50: 17953–17979
- Schrön A, Rödl C, Bechstedt F. Crystalline and magnetic anisotropy of the 3d-transition metal monoxides MnO , FeO , CoO , and NiO . *Phys Rev B*, 2012, 86: 115134
- Brown ID, Altermatt D. Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr B Struct Sci*, 1985, 41: 244–247
- Smith DL, Mailhot C. Theory of semiconductor superlattice electronic structure. *Rev Mod Phys*, 1990, 62: 173–234
- Sideris PJ, Nielsen UG, Gan Z, *et al.* Mg/Al ordering in layered double hydroxides revealed by multinuclear NMR spectroscopy. *Science*, 2008, 321: 113–117
- Barin I. Thermochemical Data of Pure Substance. New York: VCH-Cambridge, 1989

- 33 Coey JMD, Sawatzky GA. A study of hyperfine interactions in the system $(\text{Fe}_{1-x}\text{Rh}_x)_2\text{O}_3$ using the Mossbauer effect (bonding parameters). *J Phys C-Solid State Phys*, 1971, 4: 2386–2407
- 34 Li J, Zhou G, Chen Y, *et al.* Magnetism of C adatoms on BN nanostructures: implications for functional nanodevices. *J Am Chem Soc*, 2009, 131: 1796–1801
- 35 Vucelic M. Cation ordering in synthetic layered double hydroxides. *Clays Clay Miner*, 1997, 45: 803–813
- 36 Huang Y, Yu Y, Xin Y, *et al.* Promoting charge carrier utilization by integrating layered double hydroxide nanosheet arrays with porous BiVO_4 photoanode for efficient photoelectrochemical water splitting. *Sci China Mater*, 2017, 60: 193–207
- 37 Yu L, Pan X, Cao X, *et al.* Oxygen reduction reaction mechanism on nitrogen-doped graphene: a density functional theory study. *J Catal*, 2011, 282: 183–190
- 38 Greeley J, Markovic NM. The road from animal electricity to green energy: combining experiment and theory in electrocatalysis. *Environ Environ Sci*, 2012, 5: 9246–9256
- 39 Nørskov JK, Rossmeisl J, Logadottir A, *et al.* Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J Phys Chem B*, 2004, 108: 17886–17892
- 40 Bi H, Li S, Zhang Y, *et al.* Ferromagnetic-like behavior of ultrafine NiO nanocrystallites. *J Magn Magn Mater*, 2004, 277: 363–367
- 41 Battle PD, Cheetham AK. The magnetic structure of non-stoichiometric ferrous oxide. *J Phys C-Solid State Phys*, 1979, 12: 337–345
- 42 Fang Z, Solov'yev IV, Sawada H, *et al.* First-principles study on electronic structures and phase stability of MnO and FeO under high pressure. *Phys Rev B*, 1999, 59: 762–774
- 43 Gider S, Awschalom DD, Douglas T, *et al.* Classical and quantum magnetic phenomena in natural and artificial ferritin proteins. *Science*, 1995, 268: 77–80
- 44 Nørskov JK, Bligaard T, Rossmeisl J, *et al.* Towards the computational design of solid catalysts. *Nat Chem*, 2009, 1: 37–46
- 45 Greeley J, Stephens IEL, Bondarenko AS, *et al.* Alloys of platinum and early transition metals as oxygen reduction electrocatalysts. *Nat Chem*, 2009, 1: 552–556

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Conflict of interest The authors declare that they have no conflict of interest.

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超薄Ni-Fe氢氧化物纳米片作为催化剂的磁性和电子性能的条件: DFT+*U*研究

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摘要 利用密度泛函理论(DFT) + *U*方法, 本文研究了单层Ni-Fe氢氧化物纳米片中阳离子排列方式和表面补偿阴离子对其磁结构和催化性能的影响. Fe原子偏聚引起的无序结构会在纳米片中产生不同自旋排列的磁畴, 而表面补偿阴离子会影响Fe原子的局部磁矩和价态. 这两种实验条件不会从根本上改变Ni-Fe氢氧化物纳米片中磁性来源, 即磁性金属原子间的超交换作用本质, 但可在纳米片中形成特性各异的磁性超晶格. 此外, 氧还原/析出反应中间态自由能变化的计算证实最稳定磁结构的Ni-Fe氢氧化物纳米片具有优异的催化性能, 表现出磁催化剂的特性. 其原因是反应中Fe²⁺-Fe³⁺间价态的循环转变, 决定了O-H键断裂和OH基释放的难易程度, 从而控制了反应基元限制步的速率. 我们可以通过Fe离子价态变化将纳米片的磁性和催化活性联系起来, 该认识将有助于打开氢氧化物/LDHs为基的磁性催化剂设计之路.