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Oxygen evolution reaction in nanoconfined carbon nanotubes

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ABSTRACT

Improving oxygen electrochemistry through nanoscopic confinement has recently been highlighted as a promising strategy. In-depth understanding the role of confinement is therefore required. In this study, we simulate the oxygen evolution reaction (OER) on iron oxide nanoclusters under confinement of (7,7) and (8,8) armchair carbon nanotubes (CNTs). The free energies of the four proton coupled electron transfer (PCET) steps and the OER overpotentials are calculated. The Fe₄O₆ nanocluster confined in (7,7) CNT is found to be the most active for OER among the systems considered in this work. This leads to an increase in catalytic efficiency of OER compared to the hematite (110) surface, which was reported recently as an active surface towards OER. The calculated results show that the OER overpotential depends strongly on the magnetic properties of the iron oxide nanocluster. These findings are helpful for experimental design of efficient catalyst for water splitting applications.

1. Introduction

Oxygen evolution reaction (OER) is essential in many energy conversion applications, particularly the hydrogen production via water splitting [1–6]. In the field of photoelectrochemical (PEC) water splitting, the current research strongly focuses on the design of efficient electrode for OER. Hematite has emerged as a promising photoelectrode material due to its suitable band gap of about 2.1 eV, an excellent chemical stability, its natural abundance, nontoxicity, and low cost [3,7,8]. However, its low OER efficiency remains a limitation [9]. It is therefore necessary to search for the strategies for improving the OER efficiency. This study focuses on the theoretical understanding of the confinement induced enhancement of OER activity, since the improving OER through nanoscopic confinement has recently been highlighted by Doyle and Vojvodic et al. [10].

Many strategies for increasing the solar-to-fuel-conversion efficiency have been proposed [5,11–15], such as controlling of thin film thickness [5,11], doping [12], nanostructures [13–18], nanoscopic confinement [10], and altering the surface orientation [19]. Computational design at atomistic level can be achieved by the modern quantum chemical methods [20–23]. The effects of doping by Ti, Mn, Co, Ni, and Pt on the

OER overpotential have been investigated by Liao et al. [24] and Neufeld et al. [25]. Co and Ni were predicted as effective dopants for electrocatalysis of water [24]. Nguyen et al. [26], Hellman et al. [27], and Toroker et al. [28], investigated water oxidation on hematite (0001) with vacancies [28]. More recently, Zhang et al. [29] reported an overpotential of as low as 0.47 V for the hematite (110) surface with an oxygen vacancy concentration of 1.26 vacancies/nm². Neufeld and Toroker [30] studied the role of an Al₂O₃ overlayer on Fe₂O₃ for water splitting [30]. An improved water oxidation was found due to the decrease in the work function of α -Fe₂O₃ upon α -Al₂O₃ coverage that aids in extracting electrons during the water oxidation reaction [30].

CNTs have been used in many fields of scientific research [31–37]. The CNT/catalyst systems [38–41], have been studied significantly for its highly efficient OER and oxygen reduction reaction (ORR) activities. Particularly, Deng and Bao et al. [41] found that iron nanoparticles confined inside carbon nanotubes exhibit very high catalytic activities and remarkable stability as a cathode catalyst in polymer electrolyte membrane fuel cells (PEMFC) [41]. However, the effect of confinement is still not well understood.

Improving OER efficiency through nanoscopic confinement has recently been reported by Doyle and Vojvodic et al. [10]. The authors

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proposed a scheme to circumvent these scaling relationships by defining a three-dimensional nanoscopic catalyst structure that capitalizes on different interactions between the intermediates and the catalyst owing to confinement. By using density functional theory (DFT), the authors demonstrated that nanoscopic channels can selectively stabilize HOO^* relative to HO^* . These channels were shown to lower overpotential for the OER. By using DFT calculations, Zhou et al. [42] showed that the hydrogen adsorption energy on the metal surfaces is weakened by 0.12–0.23 eV when hydrogen is confined between graphene and the metal surfaces with Ni exhibiting the largest change. Thus, the authors concluded that confined system of graphene-covered Ni is an appealing effective, stable, and economical catalytic platform for hydrogen evolution reaction (HER).

Nonetheless, to the best of the authors' knowledge, reports of CNT confinement on OER activity are practically missing in the literature. Therefore, in this study, we focus on the DFT calculations of OER at iron oxide clusters confined in CNTs.

2. Methods

Density Functional Theory (DFT) calculations have been performed using the ab-initio total-energy and molecular dynamics program VASP (Vienna Ab initio Simulation Package) developed by the Fakultät für Physik of the Universität Wien [43–46]. Since Fe_2O_3 contains highly correlated 3d electrons, we chose the spin polarized DFT+U formalism [24] due to improper treatment of the d-electrons with standard DFT. The U value of 4.3 eV for Fe was derived in the literature [24] and has been applied to many hematite systems [22,25,29]. The Perdew–Burke–Ernzerhof (PBE) XC functional [47] and the projected augmented wave (PAW) [43,48] potentials were used. We use in this study a solid-gas model similarly as in other OER studies of hematite [24–26]. The simulation of photoexcitation as the driving force of the water splitting reaction has only been demonstrated for small model systems so far [49,50]. In most of the literature, water decomposition at the semiconductor surface is viewed in theoretically studies as an electro-catalytic process driven by the electrochemical potential. Thus, we use the approach developed in the literature for investigation of electrochemical water oxidation [20]. Experimental PEC water oxidation is usually operated under high pH condition, at which the surfaces are deprotonated. Thus, the initial surfaces in this study are oxygen terminated.

The theoretical overpotential is defined as the lowest potential at which all reaction steps are thermodynamically downhill. It corresponds to the difference between the required applied potential to make all reactions steps downhill and ideal catalysis.

The structure of a CNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder [51]. The way the graphene sheet is wrapped is represented by a pair of indices (n,m) . The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If $m=0$, the nanotubes are called zigzag nanotubes, and if $n=m$, the nanotubes are called armchair nanotubes. Their properties change significantly with the (n,m) values. In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behavior. In this study, we choose armchair CNTs due to the fact that they have better charge transport properties [51].

3. Results and discussion

An iron oxide cluster was optimized by DFT calculations. The effects of confinement are then studied by inserting the optimized clusters into CNTs. To keep the model simple, we choose a small cluster of Fe_4O_6 , which is two units of Fe_2O_3 . During the optimization procedure, we found two interesting geometries. Fig. 1 shows a metastable geometry with adsorbed intermediate species. The Fe atoms are located in a plane. The

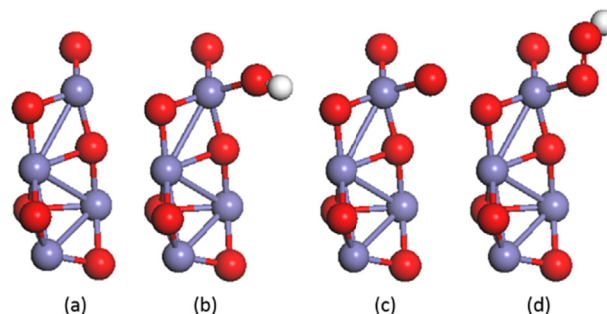


Fig. 1. The geometries of the metastable cluster, (a) the free site (*), (b), (c) and (d) with the adsorbed intermediate species, OH, O, and OOH, respectively.

Fe atom at the top of the geometry is less coordinated than the other Fe atoms. We choose therefore this Fe atom as the active site. A more stable cluster was optimized as shown in Fig. 2. Three Fe atoms are connected by Fe-Fe bonds at the bottom of the cluster. One Fe atom is connected by three Os to the Fe triangle, forming a cage-like geometry, which we call the stable cluster. The energy of stable cluster (Fig. 2 a) is 0.058 eV/atom lower than the metastable cluster (Fig. 1 a). The Fe atom at the top is less coordinated, and therefore was chosen as the active site. The intermediate species are adsorbed on the top Fe atom. The intermediate species are formed by the following reactions based on the mechanism proposed by Rossmeisl et al. [20] The four PCET steps are,



This reaction mechanism has been applied to many systems and has been shown to predict the OER activities quite well [4,21,25,52–56].

The comparison of the free energy profiles at zero bias ($U=0$ V) of the four PCET steps for the metastable cluster and the stable cluster are shown Fig. 3 (a). The stable cluster is more active for OER due to a lower overpotential (0.72 vs. 1.02 V). The intermediate species are stabilized on the stable cluster with respect to that of the metastable cluster as shown in Fig. 3. It is noteworthy that the potential determining steps are different. The potential determining step of metastable cluster is the OH formation. It is O formation for the stable cluster. Fig. 3 (b) shows the effects of a bias on the free energy profiles. The effect of a bias on all states involving an electron in the electrode is included by shifting the energy of this state by $\Delta G_U = -eU$, where U is the electrode potential relative to the standard hydrogen electrode [20]. The reaction free energies under an applied potential U are calculated as follows.

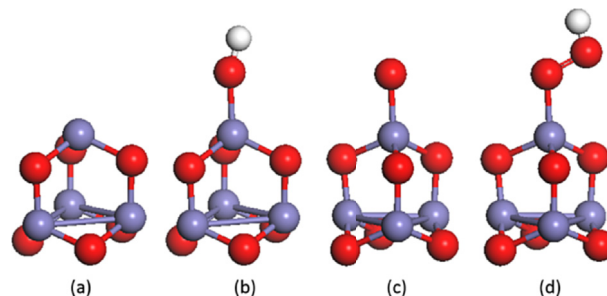


Fig. 2. The geometries of the stable cluster, (a) the free site, (b), (c) and (d) with the adsorbed intermediate species, OH, O, and OOH, respectively.

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