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The important role of oxygen defect for NO gas-sensing behavior of α-Fe_2O_3 (0 0 1) surface: Predicted by density functional theory

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ABSTRACT

Using density functional theory (DFT), we investigated and discussed the adsorption characteristics, gas-sensing response and gas-sensing mechanism of NO molecule on α-Fe_2O_3 (0 0 1) surface with and without oxygen defect (V_O). The pure and oxygen-defective α-Fe_2O_3 (0 0 1) surface exhibited opposite electron transfer. The theoretical results proved that the NO molecule acted as a donor for pure α-Fe_2O_3 (0 0 1) surface. However, it failed to explain the increasing resistance of n-type metal oxide materials. For oxygen-defective α-Fe_2O_3 (0 0 1) surface, NO molecule acted as an acceptor. The results leaded to a decreasing electron-carrier concentration, and then resulted in an increasing resistance of oxygen-defective α-Fe_2O_3 (0 0 1) surface after NO molecule was introduced into. The direction of electron transfer was reversed by oxygen defect. In addition, the V_O-NO adsorption configuration induced more stable adsorption structure and more significant electron transfer effects between NO molecule and oxygen-defective α-Fe_2O_3 (0 0 1) surface. The V_O-NO adsorption configuration would have better gas-sensing performance for α-Fe_2O_3 (0 0 1) surface.

1. Introduction

Nitrogen oxides (NO_x) gas, as main air pollutants, generate from the combustion of nitrogen and oxygen in atmosphere, such as automotive engines, power plants, etc. The appearance of NO_x gas in atmosphere has caused serious problems, such as acid rain, photochemical smog, and even endangering our health [1–4]. The detection of NO_x gas has become a research focus, especially for NO gas, due to the main component of NO_x gas is NO gas (90–95% in total) for power plants [5]. Therefore, highly sensitive gas sensors for monitoring NO_x gas became urgently required [6–10].

Traditionally, oxide sensors, which always exhibit better gas-sensing performance at higher temperatures, have been explored to detect these gases [1–3]. Lots of α-Fe_2O_3-based gas sensors, which have an accepted experimental band gap of approximately 2.2 eV [11,12], have shown advantages of multi-functions, high stability, pollution-free and low cost [13]. Metal oxides α-Fe_2O_3 have been extensively studied for potential applications, such as magnetic devices, pigments, lithium batteries, catalysts [14–19], and especially in gas sensors [20–27]. For resistive gas sensors, one important indicator is the gas-sensing response which has a strong dependence with materials' surface areas. Nano-structure materials will have better gas-sensing response than that of micro-crystalline powders due to their larger surface areas for adsorption of test gas [28–30]. Metal oxide α-Fe_2O_3 materials prepared in nano-scale will provide more sites for gas-molecules to be adsorbed on. The chemisorption of gas molecules on materials' surface leads to electron redistribution between adsorbed molecules and materials' surface. In the process of electron redistribution, some electrons transfer to adsorbed molecules (materials' surface) from materials' surface (adsorbed molecules) and then, lead to obvious variations in materials' electronic structures and resistance (conductivity) [31]. The electrons transferred in adsorption processes underlay the gas-sensing response. More electrons transfer to adsorbed molecules (materials' surface), the better materials' gas-sensing response will be. In order to improve the performance of gas sensors, we can increase the numbers of electron transfer between adsorbed molecules and materials' surface using appropriate modification methods. Previous experimental works point out the oxygen defects can improve the gas-sensing performance of metal oxides, such as SnO_2 and ZnO [32–35]. It also has been found that the oxygen defects may appear in α-Fe_2O_3 materials, especially in nano-scale α-Fe_2O_3 materials [36,37]. Thus, a fundamental understanding of atomic level interaction between adsorbed molecules and materials' surface is importance for

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improving the response of resistive gas sensors and is importance for studying the effects of oxygen defects in α-Fe_2O_3 nanomaterials.

In this paper, we investigated the adsorption characteristics, gas-sensing response and gas-sensing mechanism of NO molecules on α-Fe_2O_3 (0 0 1) surface using the density function theory (DFT) method. The adsorption structures of NO molecules on α-Fe_2O_3 (0 0 1) surface were provided after relaxation. Their relative stability between different adsorption structures was contrasted according to the adsorption energies. The theoretical results proved that the α-Fe_2O_3 (0 0 1) surface could be used as absorbent or gas sensor for NO gas. A detailed comparative study about NO gas-sensing characteristic and mechanism on α-Fe_2O_3 (0 0 1) surface with and without oxygen defect (V_O) was performed to investigate the effects of oxygen defect (V_O).

2. Theoretical method and models

The DMol^3 suit of program with density functional theory (DFT) was used to deal with the calculations [38,39]. Spin unrestricted generalized gradient approximation (GGA) pseudo-potential with Perdew-Burke-Ernzerhof (PBE) method was employed to deal with the exchange and correlation energy. In the process of calculations, the Double numerical basis sets with polarization functions (DNP) and DFT-based semi-core pseudo-potential (DSPP) were used. We used the DFT-D method proposed by Grimme to describe the van der Waals (VDW) interaction [40]. In addition, the influence of dipole moment which derived from the asymmetry of adsorption was corrected. The samplings of Brillouin zone were generated with 5 × 5 × 1 Monkhorst-Pack grid for geometry optimization and 10 × 10 × 1 Monkhorst-Pack grid for density of states (DOSs). The convergence criterions for geometry optimization, density of states (DOSs) and Hirshfeld population analysis (HPA) were 2×10^{-5} Ha for energy, 5×10^{-3} Å for displacement and 4×10^{-3} Ha/Å for force. We obtained the electron transfer between gas-molecules and materials' surface, using the Hirshfeld population analysis (HPA) method [41,42].

We employed the hexagonal structure α-Fe_2O_3 with R-3c space group for research. The G-type anti-ferromagnetic (AFM) ordering had been verified to be the ground state of α-Fe_2O_3 primitive cell [43]. The crystal structure parameters for simulation originated from previous experiment [44]. The lattice constants were a = b = 5.0351 Å, c = 13.7581 Å, α = β = 90°, and γ = 120° and its atomic fractional coordinates were Fe (0.0000, 0.0000, and 0.3553) and O (0.3062, 0.0000, and 0.2500), as shown in Fig. 1a. There were three different terminated (0 0 1) surfaces: (1) O_3-Fe-Fe layer, (2) Fe-Fe-O_3 layer, and (3) Fe-O_3-Fe layer. Previous theoretical results had proved that the Fe-O_3-Fe-R terminated (0 0 1) surface was stable than others [45]. Therefore, we cleaved the Fe-O_3-Fe-R terminated (0 0 1) surface and added a 20 Å vacuum layer to isolate the slab.

3. Results and discussion

Firstly, we studied the effect of number of repeat unit (n). One repeat unit was defined as the depth of one Fe-O_3-Fe layer containing 5 atoms, as shown in Fig. 1a. We calculated the surface energies (E_{surf}) for Fe-O_3-Fe-R terminated (0 0 1) surface with different numbers of repeat unit (n = 1, 2, 3, 4, 5 and 6), shown in Fig. 2. The surface energy was calculated as [46]:

$$E_{surf} = (E_{slab} - (n/6)E_{bulk})/A$$

where E_{surf} was the surface energy, E_{slab} was the total energy of slab, E_{bulk} was the total energy of bulk, n was the number of repeat unit and A was the total surface area of slab. The calculated surface energies were 1.29 J/m^2, 1.58/m^2, 1.62 J/m^2, 1.64 J/m^2, 1.64/m^2, 1.65 J/m^2 for n = 1, 2, 3, 4, 5 and 6, respectively. The value of surface energy for n = 5 was higher than that of surface energy for n = 4 by <0.01 J/m^2, which could be neglected. The number of repeat unit (n) had little influence on surface energy (E_{surf}) when n ≥ 4, as shown in Table 1. Therefore, we chose the 4-repeat units slab with G-type AFM ordering as our model for computational simulation, as shown in Fig. 1b.

To investigate the stability of NO molecule on α-Fe_2O_3 (0 0 1) surface, we calculated their adsorption energy (E_{ads}), define as [47]:

$$E_{ads} = E_{substrate} + E_{adsorbate} - E_{substrate-adsorbate}$$

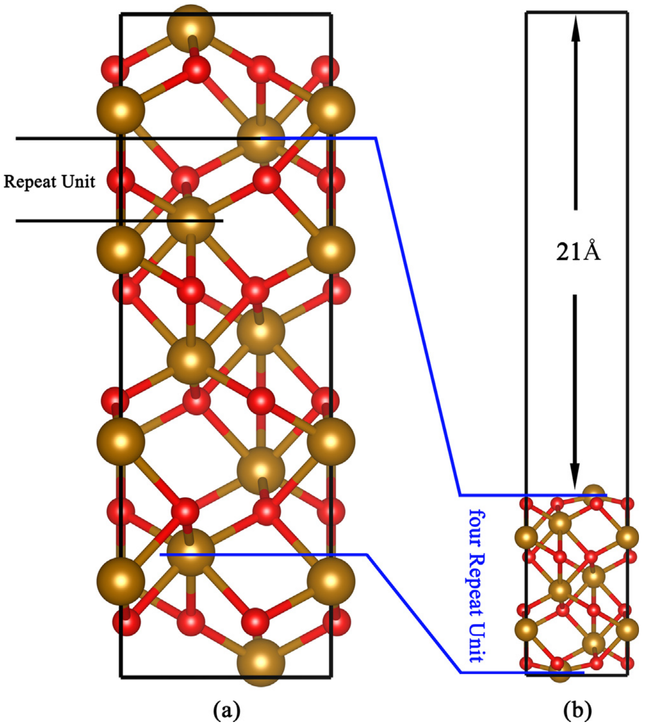

Fig. 1. The side views of (a) α-Fe_2O_3 bulk in primitive cell and (b) α-Fe_2O_3 slab with four repeat unit. Ginger and red balls represent Fe and O atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

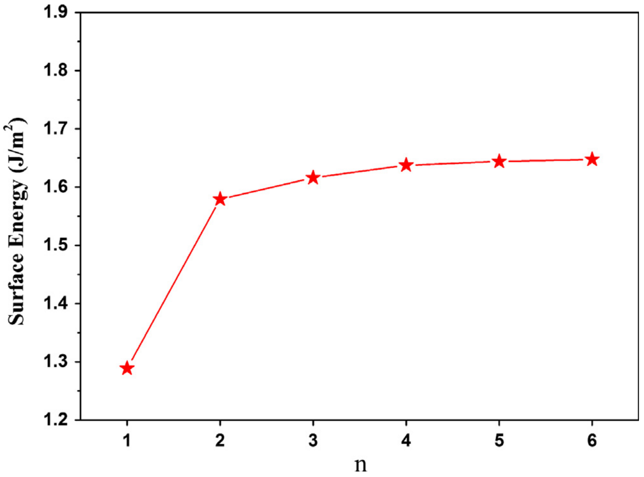

Fig. 2. The number of repeat unit (n) dependences of surface energy for α-Fe_2O_3 (0 0 1) surface.