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A DFT study on WO_3 nanowires with different orientations for NO_2 sensing application

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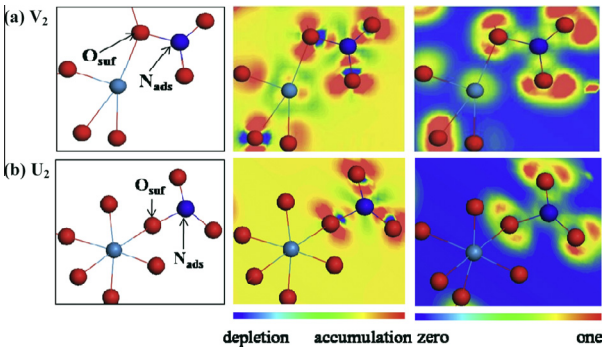
HIGHLIGHTS

- Electronic properties of NO_2-adsorbed (001)/(010) WO_3 nanowires were studied by DFT.
- Sensing mechanism was related with electronic structure and electron redistribution.
- Gas sensitivities were reflected by quantitative electron population analysis.
- Potential sensitivity levels of (001)/(010) WO_3 nanowires were suggested theoretically.

GRAPHICAL ABSTRACT

Charge density difference (middle) and ELF plots (right) of the adsorption structures of NO_2 on NW_{010} (a) and on NW_{001} (b).



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ABSTRACT

The adsorption of NO_2 molecule on the surface of WO_3 nanowires with [001] and [010] orientations were investigated using density functional theory (DFT) calculations with aim to explore their potential sensing abilities theoretically. It is found that NO_2 molecule can adsorb in multiple stable configurations for the WO_3 nanowires with the two orientations, and the NO_2 adsorption on the surface tunes the electronic structures of WO_3 nanowires, giving rise to new impurity electronic states and then changing the band gap and the Fermi level position. The sensitive electronic structures as well as the multiple stable configurations to NO_2 adsorption highlight the potential of WO_3 nanowires as a sensor to detect NO_2 gas. Further calculations about the atomic Mulliken charge population, planar averaged charge density differences, and electron localization functions (ELF) indicate that NO_2 adsorption on [010]-oriented WO_3 nanowire induces much stronger adsorbate-surface interaction and much more electrons extracted from the surface than on [001] nanowire, hinting a much higher sensitivity expectable for a NO_2 gas sensor based on WO_3 nanowire with [010] orientation.

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Introduction

Detection of gas molecules relevant to chemical and biochemical processes is of critical importance in environmental, industrial, and medical monitoring. For instance, toxic NO_2 gas resulted from combustion and automotive emissions is a main source of acid rain and photochemical smog [1], and the detection of NO_2 is therefore very important for both environmental protection and human health. It has been found that resistive-type sensors based on metal oxide semiconductors are well-suited for this purpose owing to their remarkable gas sensing performance and simple structures

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[2,3]. Extensive researches on various metal oxide semiconductors have illustrated that tungsten oxide (WO_x), which is a wide band-gap n-type semiconductor, is a promising material for detection of toxic NO_2 gas [4–6].

Among the series of tungsten oxides, WO_3 and $W_{18}O_{49}$ are the most important for sensing application and are reported to be readily experimentally synthesized. It has been proved that monoclinic WO_3 and $W_{18}O_{49}$ nanowires can be successfully grown using hydrothermal/solvothermal synthesis or thermal evaporation process [7–10], and appropriate thermal treatment can result in the successful transformation between WO_3 nanowire and $W_{18}O_{49}$ nanowire [11,12]. Due to their unique structural characteristics, such as large specific surface area, single crystalline structure and dimensions comparable to Debye length, one-dimensional tungsten oxides have exhibited much good performances in term of high sensitivity, low operating temperature, and long-term stability in detection of dilute NO_2 gas [7,13,14].

The conventional sensing mechanism of semiconductor oxide gas sensors belongs to the surface-controlled type, that is, surface adsorption of gas molecules induces the electrical conductivity change of the oxides [15]. To develop the high sensitive gas sensor, it is necessary to theoretically understand the microscopic mechanism of conductivity variation induced by surface-adsorbate interactions on the gas-adsorbed nanowire at atomic level. Some efforts have been made in this aspect. For instance, the ab initio study of the NO and NO_2 adsorption processes on (110) SnO_2 surface provided theoretical hints for the development of improved NO_x gas sensor [16]. The ab initio simulations for adsorption of NO_x on different types of ZnO surface preformed by Yarovsky et al. [17,18] tried to clarify the gas-sensor interaction and found that the adsorbates behave as electron acceptors, withdrawing charge from the surface. As to the study about tungsten oxide-based gas sensors, however, relatively rich experimental works at present show the lack of the correlative theoretical studies, and only very limited works can be found in the literatures. Oison et al. [19] illustrated the microscopic mechanism of O_3 and CO sensing on WO_3 surface by highlighting the role of the oxidation of CO and the reduction of O_3 on the value of the resistivity of WO_3 gas sensor. Our group has previously used DFT calculations to investigate adsorption of NO_2 on bulk WO_3 (002) surface [20]. Recently, we investigated the effect of NO_2 adsorption on the electronic structure and electron population of [010]-oriented $W_{18}O_{49}$ nanowire employing DFT method [21]. Such theoretical studies are highly important to in-depth understand the gas sensing mechanism of nanowires argued based on the experiment phenomena for the purpose of exploring new type of sensing materials with high sensitivity to NO_2 gas.

One-dimensional (1D) tungsten oxide nanowire can grow along different crystal directions, depending on the growth process and parameters controlling. To theoretically explore the discrepancy in sensitivity and potential of tungsten oxide nanowires with different orientations for sensing application, in this work, we focus on first-principle calculations of the adsorption of a single NO_2 molecule on the surfaces of WO_3 nanowires with different orientations. To avoid the calculation deviation due to irregular structures of unsaturated WO_x, stoichiometric WO_3 with strict periodic structure is chosen to construct the nanowire model. The adsorption energy, electronic structure, atomic Mulliken charge population, charge density differences and electron localization functions (ELF) are calculated. Particular attention is paid to understanding the modification of electronic structures and the quantitative feature of charge transfer with aim to provide the theoretical understanding for NO_2 sensing mechanism of WO_3 nanowire-based sensor and theoretical hints for the development of high sensitive NO_2 gas sensor using tungsten oxide nanowire as the base sensing material.

Calculation and modeling

Modeling system

To construct model of 1D nanowire, a supercell method was employed. The initial model of crystalline WO_3 nanowire was constructed by cutting the supercell of monoclinic WO_3 structure with a virtual cylinder, as shown in Fig. 1(a) and (b). All W and O atoms outside the cylinder were removed to achieve the WO_3 nanowires. According to the previous experimental results [22–24], WO_3 nanowires usually grow preferentially along the *b*- or *c*-axis, so the direction of the cylinder was chosen to produce wires with [001] and [010] growth direction, and the [001]- and [010]-oriented WO_3 nanowire models were respectively marked as NW_{001} and NW_{010}.

Experimentally, the general diameter of as-synthesized single tungsten oxide nanowire is about several nanometers and the minimum value ever reported is 1 nm [25–27]. In this work the constructed nanowires have the diameter of about 1 nm. To eliminate the interaction between neighboring nanowires, a vacuum space in the thickness of 20 Å was added along the transverse directions of [001] and [010] nanowires. A convergence test for a vacuum space of 25 Å in thickness showed unnoticeable change in

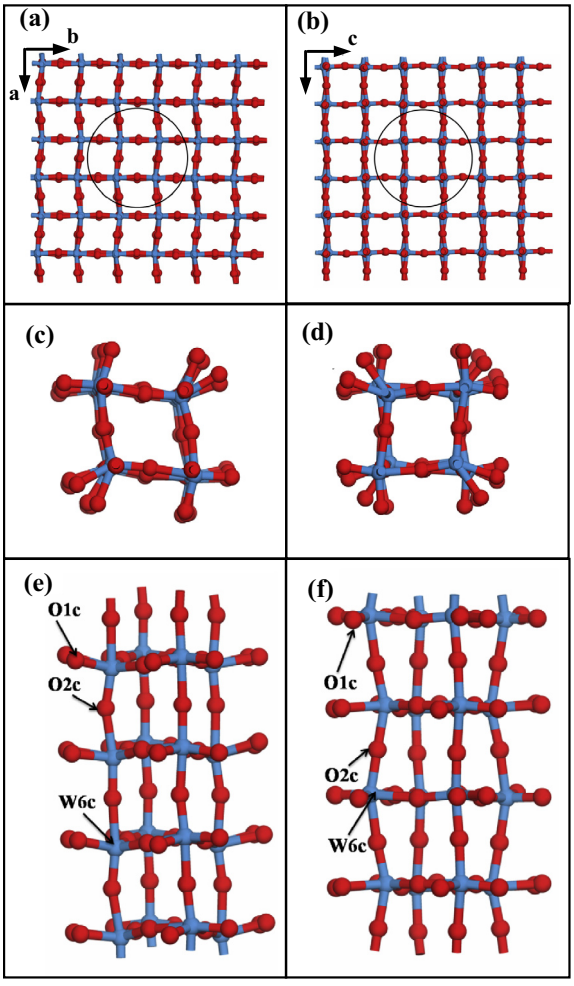

Fig. 1. (a and b) $5 \times 5 \times 5$ WO_3 supercells with monoclinic structure used for constructing [001]-and [010]-oriented nanowire models; (c and d) top views of the optimized nanowires NW_{001} and NW_{010}; (e and f) side views of NW_{001} and NW_{010}. The O and W atoms are respectively represented by red and light blue balls. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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