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Research paper

Electronic transport properties and CO adsorption characteristics on TiO_2 molecular device – A first-principles study

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ABSTRACT

The transport and CO adsorption properties on rutile TiO_2 molecular device is studied using DFT method. The transport characteristics of TiO_2 nanostructure are described in terms of electron density, density of states and transmission spectrum. The applied bias voltage in TiO_2 device increases the peak maxima in the valence band as well as in the conduction band. The electron density in TiO_2 nanostructure is found to be more along oxygen sites than in titanium sites. The transmission spectrum of TiO_2 molecular device provides clear insights on transmission of electrons at various energy intervals. The adsorption properties of CO on TiO_2 molecular device is studied in terms of voltage and resistance characteristics along the scattering region. The findings of the present study give a clear vision on improving the electronic transport and CO adsorption properties on TiO_2 molecular device, which can be used as CO sensor.

1. Introduction

The emission of hazardous gas contaminants from industrial, residential and commercial places causes severe risk to human life. The environmental monitoring plays a significant role in controlling the pollutants. Generally, a variety of analytical techniques are utilized to sense the hazardous gas in the environment in the order of parts per million (ppm). The analytical techniques require sophisticated instruments and knowledge in interpreting the results obtained from the analysis. Moreover, the solid state gas sensors are good substitute to detect the contaminant in ppm range [1]. Titanium dioxide (TiO_2) is one of the most significant transition metal oxides, which receive great attention owing to its excellent stability, chemical inertness, low cost and non-toxicity among the solid state semiconductor devices [2,3]. TiO_2 belongs to n-type semiconductor with wide band gap of 3.23 eV [4–7]. In addition, TiO_2 exhibits different polymorphs namely brookite, n-TiO_2, rutile and anatase phases [8,9]. In the past few decades, TiO_2 has been elaborately investigated both experimentally and theoretically. Moreover, TiO_2 exhibits excellent physical and chemical properties [10], which can be used as electrochromic, antifogging, biomedical coatings, pigments, paints, chemical sensors, dye-sensitized solar cells and photocatalyst [11–15]. The properties of TiO_2 can be greatly enhanced with the substitution of impurities and also through creating defects in the nanostructure [16,17]. The literatures show that there are many reports in studying the photocatalytic property of TiO_2 with the incorporation of impurities such as Pd [18], Au [19], Pt [20,21], and Hg [22]. The nanostructures and their various properties of TiO_2 have been extensively studied in order to improve their sensing performance towards carbon monoxide (CO) [23–28]. Even though TiO_2 exhibits in three different phases, rutile TiO_2 possesses tetragonal structure and rutile phase is more stable at most temperatures and pressures up to 60 kbar than anatase and brookite phases. TiO_2 is also thermodynamically favourable phase. The rutile phase grows much faster than other phases. Zhang et al. reported that both anatase and brookite phases transforms to rutile phase after a certain particle size [29]. Furthermore, rutile TiO_2 is more stable than anatase phase for particle size greater than 14 nm [30]. The rutile TiO_2 nanotubes exhibit different optoelectronic properties compared to other phases [30]. The motivation behind the present work is to investigate the rutile TiO_2 nanostructure and to improve the CO adsorption properties of TiO_2 nanostructures. The detection of trace amount of CO toxic gas using TiO_2 base material will alert the personnel working in a toxic environment. The threshold limit for CO as per Occupational Safety and Health Administration (OSHA) is 50 ppm averaged over eight hours work shift [31]. Beyond the threshold limit, CO may cause harmful effects on humans. In this work an attempt has been made to investigate CO adsorption properties on rutile TiO_2 molecular device.

2. Computational methods

The first-principles calculation on rutile TiO_2 molecular device are carried out by density functional theory (DFT) method facilitating TranSIESTA module in SIESTA package [32]. TiO_2 nanostructure is optimized by decreasing the atomic forces on the atoms to be smaller

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than 0.05 eV/Å. The generalized gradient approximation (GGA) combined with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional is utilized to investigate the electron-electron interaction [33, 34]. The Brillouin zones are sampled with $1 \times 1 \times 50$ k points. The CO adsorption characteristics on TiO_2 nanostructures are carried out with the help of SIESTA package, in which the core electrons are substituted suitably by Troullier-Martins pseudopotentials for titanium and oxygen atoms. Further, the electronic wave function of titanium and oxygen atoms are expanded in terms of its basis set, which mainly depends on the numerical orbitals. The optimization of TiO_2 nanostructure is supported with double zeta polarization (DZP) basis set for both the electrodes and scattering region in the present study [35]. In order to study the electronic properties of TiO_2 and to exclude the interaction of TiO_2 nanostructure with its periodic images, 10 Å vacuum padding is modelled along *x* and *y* axes. This facilitates the computation process while analyzing the density matrix Hamiltonian. The atoms in TiO_2 nanostructure freely move along their positions until the convergence force lesser than 0.05 eV/Å is achieved.

3. Results and discussion

3.1. Structure of TiO_2 nanostructure

The TiO_2 nanostructure device is built with the help of International Centre for Diffraction Data (ICDD) Card number: 89-4202, which exhibits tetragonal structure [36]. In the designed TiO_2 molecular device, there are three regions, namely right electrode, scattering region and left electrode. The scattering region of the TiO_2 molecular device consists of TiO_2 nanostructure placed between two electrodes. The width of the scattering region is around 10.430 Å and the width of the left and right electrode is 1.946 Å. TiO_2 nanostructure is repeated thrice along a and b-axis each and five times along *c*-axis. Along TiO_2 scattering region, a potential difference is maintained between the right and left electrodes for the flow of current. The scattering region of TiO_2 nanostructure consists of fifty four titanium atoms and hundred and eight oxygen atoms. The region on the right and left electrodes include eighteen titanium atoms and thirty six oxygen atoms each. The potential difference of $+V/2$ and $-V/2$ is maintained across the left and right electrode through TiO_2 scattering region. A potential difference from 1.4V to 3V in step of 0.2V is varied between left and right electrode. Moreover, the variation in the bias voltage leads to the change in transmission and density of states along TiO_2 molecular device. Fig. 1 refers to the schematic diagram of TiO_2 molecular device.

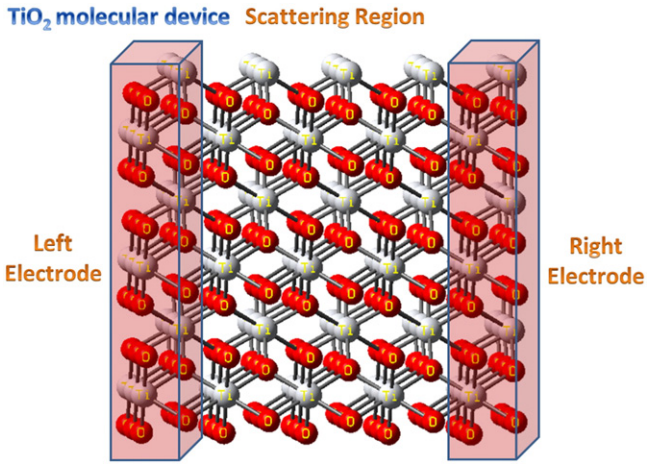

Fig. 1. Schematic of TiO_2 molecular device.

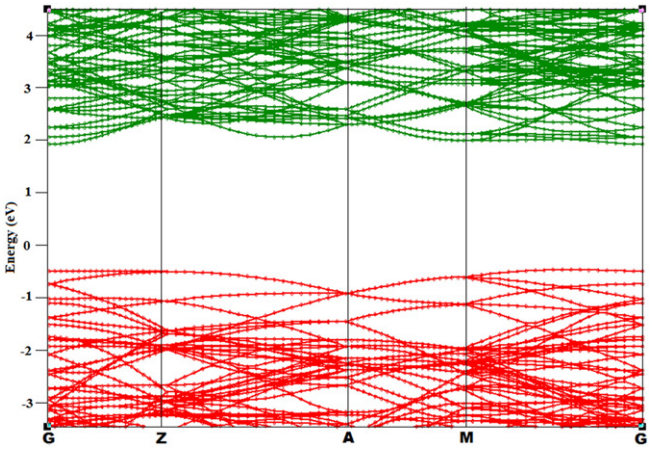

Fig. 2. Band structure of TiO_2 nanostructures [G - gamma point-Center of Brillouin Zone (0, 0, 0), Z - Center of a square face (0, 0, 0.5), A - Corner point in simple tetragonal (0.5, 0.5, 0.5), M - Center of an edge (0.5, 0.5, 0)].

3.2. Band structure of TiO_2 nanostructures

The band structure throws the light on the materials properties of TiO_2 nanostructures. Moreover, it confirms the insights on nanostructures, whether the material possesses semiconducting or metallic properties. Fig. 2 depicts the band structure of TiO_2 nanostructures [G - gamma point-Center of Brillouin Zone (0, 0, 0), Z - Center of a square face (0, 0, 0.5), A - Corner point in simple tetragonal (0.5, 0.5, 0.5), M - Center of an edge (0.5, 0.5, 0)]. The band gap may be calculated along the gamma point (G) in the band structure diagram. It is observed

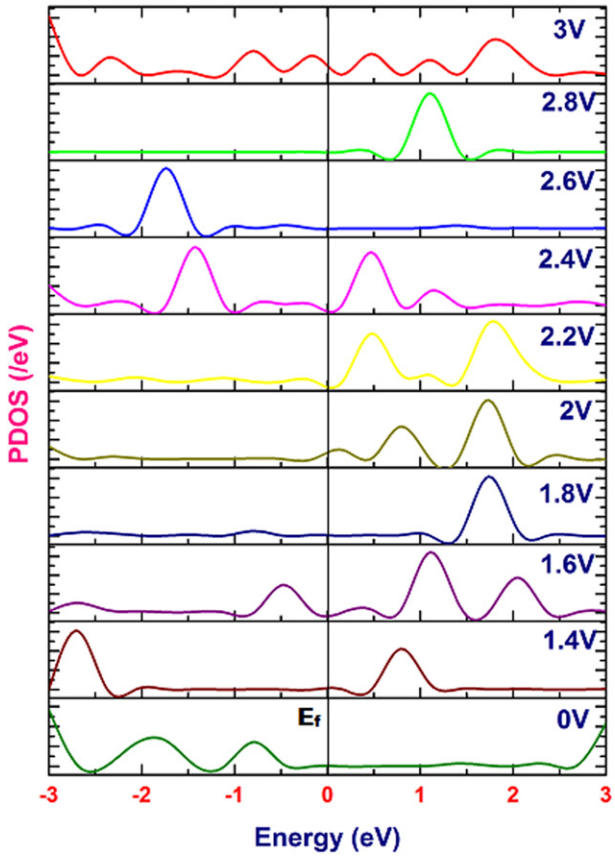

Fig. 3. PDOS of TiO_2 nanostructure.