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Structural, electronic and optical properties of CO adsorbed on the defective anatase TiO_2 (101) surface; a DFT study

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ABSTRACT

This paper illustrates the study of stable structural, electronic and optical properties of carbon mono oxide (CO) molecule adsorbed on pure anatase TiO_2 (101) surface and CO molecule adsorbed on defective anatase TiO_2 (101) surface containing oxygen (O) atom subsurface vacancy using first-principles study calculations based on density functional theory (DFT) method. A foreign molecule CO was added in the interstitial space of anatase TiO_2 (101) surface. It was observed that, adsorption of CO molecule is not favorable on pure anatase TiO_2 (101) surface, however adsorption process is improved when subsurface contains O atom vacancy defect. In case of anatase TiO_2 (101) surface containing subsurface vacancy, adsorption process is exothermic, resulting in stable structures. The adsorption energies calculated for CO molecules adsorbed at O_{2c} site, at defect site and at Ti_{5c} site of anatase surface containing subsurface O vacancy are 0.16 eV (at O_{2c}), 0.32 eV (at defect site) and 0.43 eV (at Ti_{5c}) site. DOS and PDOS plots are calculated for all the structures. Results indicated that CO molecule adsorption introduces surface states at the Fermi energy level (E_F) as shown in partial density of states (PDOS) plots. The dielectric matrix and absorption coefficient (α) for defective anatase TiO_2 (101) surface, CO adsorbed at O_{2c} site, at defect site and at Ti_{5C} site of anatase TiO_2 (101) surface containing O atom subsurface vacancy has been calculated within the random phase approximation (RPA) using VASP (Vienna *ab-initio* simulation package) code. It was observed that upon CO adsorption at defective anatase surface, real and imaginary dielectric function peaks were shifted towards lower energy level and a small absorption peak was observed at 1.1 eV energy level which is not present in case of defective anatase (101) surface. CO adsorption produces a red shift in the absorption spectrum of anatase TiO_2 (101) surface containing subsurface O atom vacancy.

1. Introduction

The production of toxic waste gases from commercial, industrial and residential places has become a meticulous threat to human life. The task of environmental monitoring plays crucial role for controlling the pollutants. There are numbers of analytical techniques which are used for detecting toxic gases present in the environment. In addition to that we are in dire need of smart gas sensor technology to detect the pollutant particles in parts per million [1]. Titanium dioxide (TiO_2) is under immense attention nowadays due to its excellent structural stability, low cast, chemical inertness, large surface area and non-toxic nature among other semiconductors [2,3].

Titanium dioxide (TiO_2) also known as titania is one of the most important n-type wide band gap semiconductor. J.K Burdett et al. [4] conducted experimental studies on anatase and provided band gap value for Titanium dioxide around 3.23eV. According to Xi Pan et al. [5] and C. C. Yen et al. [6], theoretical band gap value of TiO_2 is reported to be 2.16–2.27eV. Titanium dioxide TiO_2 has four different polymorphs namely n-TiO_2, brooklite, rutile and anatase. Among these polymorphs anatase is treated promisingly because of its importance in photocatalytic degradation of environmental pollutants. An intensive study has been carried out on anatase surfaces during past decade and it is discovered that anatase (101) surface is the most stable surface followed by anatase (100) and anatase (001) [6,7].

Anatase TiO_2 is a promising agent to detect CO gas present in

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environment that's why various approaches have been used to determine the adsorption of CO on anatase TiO_2. Raina Wanbayor and Vithaya Ruangpornvisuti [7] used density functional theory calculations to investigate the adsorption of CO, H_2, N_2O, NH_3 and CH_4 gases on anatase TiO_2 (101) and (001) surfaces. Their calculations showed that H_2 dislikes to adsorb while N_2O adsorbs energetically on anatase surface. They also discovered co-adsorption of N_2O and CO on anatase surfaces. Qili Chen et al. [8] conducted a research on electronic structure of Sulphur (S) and Carbon (C)-doped Anatase (101) surfaces using DFT method and found that complex of anion and cation doping configuration formed easily in the most range of O chemical potential for both S and C doping. Feng Qing et al. [9] conducted NO molecule adsorption study on anatase (101) surface and discovered that adsorption is higher on the surface containing O vacancy defects and an absorption peak is observed in low energy region corresponding to an energy of 0.9 eV. Previously, most of the work is done to observe the adsorption of different molecules at anatase (101) surfaces without any defects present on the surface and it is observed that, no effects appear on electronic and optical properties of anatase surface after CO adsorption. However a less amount of studies are attributed to CO adsorption at anatase (101) surface containing O atom subsurface vacancy. As described earlier by Feng Qing et al. [9] that, the adsorption process is increased with presence of O vacancy defects in the surface, for that reason we adopted a new approach for O atom subsurface vacancy to determine the effects of CO adsorption on electronic and optical properties of defective anatase (101) surface. In this paper an attempt has been made to determine electronic, optical properties and stable structures of anatase (101) nanostructure surface after molecular adsorption of CO using first-principles density functional theory (DFT) method and the results are reported.

2. The model structure and computational details

All our first-principles calculations were performed by means of VASP (Vienna *ab-initio* Simulation Package) [10] code which uses projector-augmented-wave (PAW) formalism. Perdew-Burke-Ernzerhof (PBE) [11] exchange-correlation (XC) functional of the generalized gradient approximation (GGA) was employed for all our calculations which is shown to be very effective for cluster [12] and surface calculations [13,14]. In order to guarantee an effective computer calculation ability and reliability, the energy convergence standard is set to 2×10^{-5} eV/atom, the plane wave cut-off energy is fixed at 400 eV and a regular Monkhorst-pack grid of $7 \times 6 \times 1$ k points were adopted.

According to previous surface studies [8,9,15,16], the most stable anatase TiO_2 (101) surface contains an outermost layer which terminates at two-coordinate O (O_{2c}), followed by a second layer of five-coordinated Ti (Ti_{5c}) and a third layer of three-coordinated O (O_{3c}) atom. A 6-layer surface structure model with a vacuum thickness value of 10 Å was established, 1×2 super-cell is built and conditions are optimized. The surface structures before and after optimization are shown in Fig. 1(a) and (b) respectively. During optimization process, atoms present at the surface undergo relaxation, but no reconstruction phenomenon appears. After the relaxation of surface structure, outermost layer still terminates at O_{2c} but sub-layer becomes O_{3c} and third layer is converted into Ti_{5c} atom as shown in Fig. 1(b). The 1×2 super-cell model acts as adsorption substrate on which CO molecules are built and the resulting structure is then geometrically optimized. After Optimization, the CO molecular bond length is determined to be 1.252 Å. In this paper different ways of adsorbing CO molecule onto TiO_2 (101) surface are discussed.

3. Results and discussions

3.1. Adsorption of CO on anatase TiO_2 surface without any O vacancy

We selected following three adsorption sites from which the calculation models were constructed:

(i) Vertical adsorption of CO with C ending above the O_{2c} of the complete anatase TiO_2 (101) surface as shown in Fig. 2(a);
(ii) Vertical adsorption of CO with C ending above the O_{3c} position as shown in Fig. 2(b);
(iii) Vertical adsorption of CO with C ending above the Ti_{5c} position as shown in Fig. 2(c);

According to results provided by Jessica Scaranto and Santi Giorgianni [17] on surface adsorption of CO on anatase TiO_2 surface, the C atom of CO molecule gives rise to shorter C–O bond length and Larger C–Ti bond length). Typical geometry before relaxation of structure of CO molecule adsorption at different sites of anatase (101) surface is shown in Fig. 2(a–c) and the geometry after relaxation of CO molecule adsorption at different sites of anatase (101) surface is shown in Fig. 3(a–c). Comparison between Figs. 2(a) and 3(a) reveal that the C–O_{2c} bond length changes from 1.250 Å to 1.190 Å along with O_{2c}-Ti_{6c} changing from 1.930 Å to 2.867 Å, comparison between Figs. 2(b) and 3(b) reveal that C–O_{3c} bond length increases from 1.199 Å to 1.387 Å and comparison between Figs. 2(c) and 3(c) reveal that C–Ti_{5c} bond length increases from 1.493 Å to 2.346 Å, respectively. These structural parameters calculated for relaxed anatase TiO_2 (101) surface are in complete agreement with the previous studies available [15–17], which indicates that our calculation model and methods are accurate enough. First case of CO adsorption at O_{2c} reveals that CO molecule with vertical adsorption on O_{2c} tries to reduce the distance by attracting O2c atom outwards. However in case of CO adsorption at O_{3c} and Ti_{5c} atoms, CO molecules adsorptions after relaxation process, occur away from the surface substrate, thus indicating weak adsorption on the surface.

3.1.1. Adsorption energy

According to You Han et al. [18] the adsorption energy of the CO molecules on the anatase TiO_2 (101) surface is defined as follows:

$$E_{ads} = (E_{substrate} + E_{CO}) - E_{(CO+substrate)} \quad (1)$$

where E_{ads} is the adsorption energy of surface, $E_{substrate}$ represents the total energy of the bulk anatase TiO_2 (101) surface, E_{CO} is the molecular energy of CO before adsorption process and $E_{(CO+substrate)}$ is the entire energy of complete surface with CO molecule after adsorption. Table 1 list the adsorption energies of the system when CO molecule is adsorbed at different sites of pure anatase TiO_2 (101) surface without any vacancy present on surface.

From the values of adsorption energies one can clearly see that E_{ads} of CO molecule adsorbed at O_{2c} and O_{3c} sites have negative values, suggesting that adsorption processes are difficult to take place naturally. However, when CO molecule is placed on top of Ti_{5c} site, it has very little positive value for E_{ads} indicating that the adsorption process is exothermic. However very low positive adsorption energy E_{ads} suggests that it is not most suitable model for adsorption of CO molecule. These obtained results are consistent with previous studies [15–17].

3.1.2. Surface electronic structure

Spin polarized total density of states (TDOS) and projected density of states (PDOS) plots for anatase TiO_2 (101) surface after