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Research Paper

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Slabs of Crystallographic Planes of Rutile TiO_2 as a Photocatalytic Surface

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***Abstract*—** This study is initially dealing with the density of states of the rutile TiO_2 system and then dealing with the system made from the crystallographic plane in term of the slab. Four slabs (corresponding to the planes (110), (101), (211) and (301)) had been chosen for the study. These slabs assumed to be having the free surfaces of its solid and involved in a catalytic activity as a photocatalyst. The nature of such surfaces as a catalyst has been studied from their electron density of state in this paper. The variation in Band gap and nature of DOS was found significantly different. The work has reported (110) plane surface would be better compare to other as a free surface for the application as a photocatalyst.

Keywords— *Photocatalyst slab, DFT, Density of states, Energy band gap, slabs of rutile TiO_2*

I. INTRODUCTION

The TiO_2 is widely used as photo-catalysts due to their high surface area, robustness, low-cost, abundance and non-toxicity. Under UV irradiation, Ti act on particles to produce free radicals in aqueous solution, which had degraded organic fluid in water. The role involves degradation of pollutants [1] in atmosphere, virus, bacteria[2], germs, micro-organisms [3]. Under the pouring of water, it cleans this degraded waste on it quickly due to hydrophobic micro-structural surface morphological properties at smaller dimensions[4], [5]. This makes TiO_2 more environmental friendly and natural cleaner. However, the contact angle of water droplet on a TiO_2 surface is considerably influenced by the temperature variations and suffers wettebility [6]. Among the naturally occurring polymorphs (rutile, brookite, anatase etc.) of TiO_2, the rutile has found the stable form at high temperature and pressure in kinetic and thermodynamic studies [7], [8] and [9]. Rutile's crystal structure was determined by Vegard [10] and refined by various researchers. The Rutile TiO_2 has tetragonal crystal structure, space group number 136 D_{4h14} – P42/mnm (H-M symmetry) with Hall symmetry '-P 4n 2n'. Number of atoms in a cell are 6 in which two are Ti and four are O. Ti has 12 and O has 6 valance electrons. In pure phases, anatase was reported better photocatalytic activity[11]. But it is not the whole truth. These two polymorphs show varying photo-activity, as well as the same material with different crystallographic orientations exhibit different activities [12]–[17].

In a catalytic applications, the surface of the catalyst played crucial role. The importance of the influence of atomic arrangements of rutile TiO_2 in (001), (100) and (110) surfaces have been reported for catalytic and photocatalytic application [18]–[20]. The absorption edge of with dominant {101} and {010} facets are nearly overlapped (i.e. very close bandgaps indication of {010} and {101} facets) and therefore the bandgaps of facets satisfy the order {101} ≈ {010} > {001}[21]. Here the bandgap can the key, where the catalyst can be more active for the visible range of light spectrum. In "Facet Engineering of TiO_2 Nanocrystals for Solar Energy Conversion", Jian Pan nicely investigated few surfaces [17]. The work on (301) and (211) has not been found in literature of TiO_2 rutile especially in term of the density of state of an electron. However, the (211) surface of anatase is reported a high reactivity surface and reveal that water molecule can be easily dissociated on a Ti^{4+} [22], similarly adsorption of selected ions on (101) surface [6].

The density state of electrons of material is responsible to have different physical and chemical properties of the material. The simulated structural and physical properties of the four polymorphs of TiO_2 are studied by Masanori Matsui [23]. If the surface of the catalyst material has the same plane then each plane's surface may have some difference in their electronic density of state which can be use to increase an efficiency of material by applying the layer of material with its crucial plane as on its surface. In a present work, we systematically studied this using DFT method and confining our focus on the (110), (101), (211) and (301) planes. For

this, the paper has been organized as follows. In a second section, the details of selected TiO_2 rutile system and the concerned computational details has been given after the first section of introduction where the background was discussed. The calculations, results are mentioned and discussed in details in latter section of Results and Discussion. The paper has concluded in the 'Conclusions' section which is followed by References.

II. System and Computational Methodology

We have performed all calculation using Quantum espresso software packages [24]. The scf calculation PWSCF program was used for the system with 48.00 number of electrons (up: 24.00, down: 24.00), 42 number of Kohn-Sham states. The kinetic-energy cutoff and the charge density cutoff were selected 51.6784 Ry and 575.4520 Ry for all systems in this paper. Ultrasoft pseudo-potentials (PP) with GGA-PBE exchange-correlation has been selected which were obtained from the Quantum Espresso site. We use Ti.pbe-spn-rrkjus_psl.1.0.0.UPF, O.pbe-nl-rrkjus_psl.1.0.0.UPF PP. An MPI Parallelization was run for single thread four core processors. The data from AMCSD database code 0005164 [25] was used to initiate the study. The lattice parameters of the system are 4.59300, 4.59300, 2.95900 (A), 90°, 90°, 90° and volume is 62.422 $Å^3$ with an experimental density 4.250 g/cm^3. Four slabs of higher intensity planes were designed for the width one and for the low vacuum. The slabs were made by using open source GUI program BURAI-1.2. Their appearance is shown in Fig.1 and modified parameters are given in a Table1.

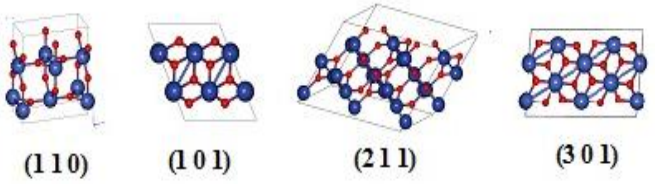

Figure 1: Illustration of slabs for rutile TiO_2 (upper surface in the direction of plane)

Table 1: Slab model made changes in a single crystal of rutile TiO_2 (a, b, c in Å and α, β, γ in deg. units)

Name	Bravais Lattice	a (Å)	b (Å)	c (Å)	α (deg.)	β (deg.)	γ (deg.)
(2 1 1)	Triclinic	1.09	7.49	9.17	93.8	71.6	115
(1 0 1)	Triclinic	4.59	5.46	6.82	114.0	90.0	90.0
(3 0 1)	Triclinic	4.59	9.99	6.40	84.6	90.0	90.0
(1 1 0)	Orthorhombic	2.96	6.50	7.44	90	90	90

III. Results and Discussion

A. Ground state of TiO_2 original system

The ground state calculations have converged in 13 iterations in the both scf and non-scf calculations (for dense k-grid). The details of the non-self consistency field calculation for the 25° TiO_2 has been summarized in table1. The non-scf fermi levels slightly different fermi energy which wasn't seen in scf calculation (10.4318 for both up-spin and down-spin). However magnetization appears zero value for convergence.

Table 2: non-scf run extracted parameter for 25° TiO_2

Output parameters	non-SCF
Temperature	25° TiO_2
E_f up (eV)	9.144
E_f down (eV)	9.142
Total Magnetization μB/cell	0
Highest occupied (eV)	9.1440
Lowest unoccupied (eV)	11.0348
E_g (eV)	1.8908

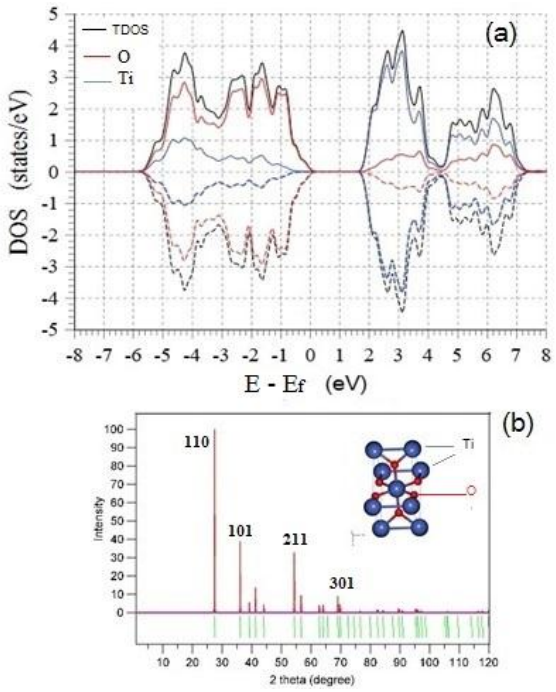

Figure 2: (a) DOS of a TiO_2 (at 25°). Colour of the plot indicates Black-total TiO_2, Red-Oxygen and Blue Titanium. (b) Corresponding X ray diffraction peaks (plotted using VESTA) with a unit cell of TiO_2.

B. Density of states and Band gap for photocatalyst

TDOS illustrated the difference in density of electron's density of states below valance band. In (110) and (301) cases, the localized states were found splitting between -20eV to -40eV. Except localized in (211) case, TDOS has broaden in (110) and found splitting in (101) and (301) cases. Fermi level is found at the center of highest valance band and lowest of the conduction band in (211), which exhibits highest energy gap (E_g) compare to other slab cases. However in a (110), gap mostly nullified. All these outcomes

have been shown in Fig.3 and Fig.4. Fig. clearly illustrated the E_g details. HRSTM Analysis by Anders Ronnau, found a highly anisotropic, long-range repulsive pair potential which describes the interaction between single pairs of vacancies on the (110) surface of the TiO_2 [26].

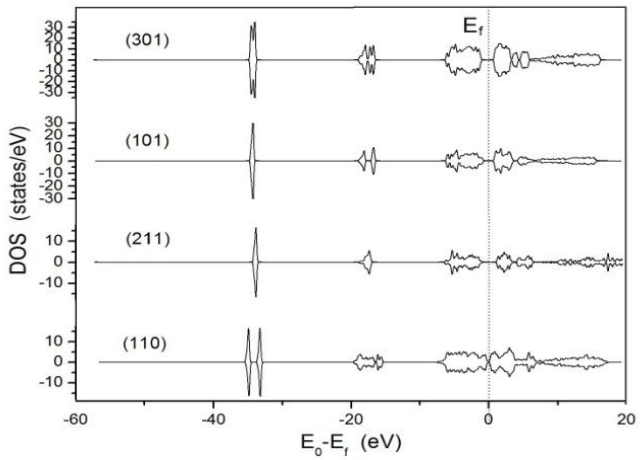

Figure 3: TDOS for different slab model

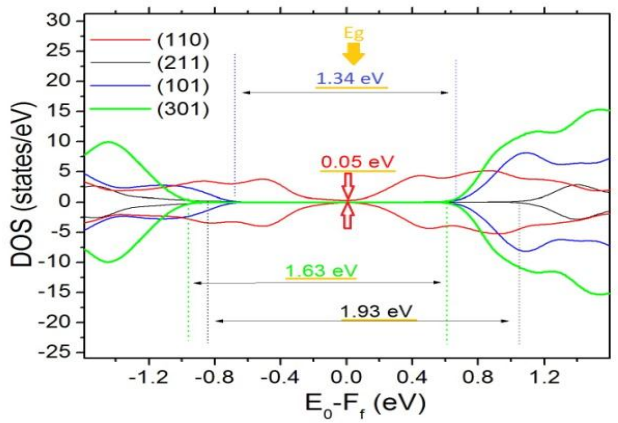

Figure 4: E_g illustration from DOS corresponding to free surface of slabs (110), (211) and (301)

The vacancies active sites are on the (110) surface (see Fig.1). Anders Ronnau has quoted that "if these vacancies were to form vacancy islands, they would most likely reconstruct into a less reactive structure" [26]. Fig.4 shows symmetry in spin-up and spin-down of the density of electron state implies that the Oxygen vacancies were not formed, more correctly it was taken automatically during the selection of slab and it can be variable in actual practice. But Inner orbital seems clear splitting in its DOS. The core orbitals seem affected largely in (110). Our focus is actually on the surface in this work.

Generally, UV light activates the formation of positive ions on the surface of TiO_2. The decrease in band gap is the indication of red shift to occur in the process of absorption of light energy. We can say that the activation light energy is now reduced. Red shift can be understood as; the molecular orbitals remain no more in a localized in this Millar cut plane of the surface. If this is not wrong, then the (110) plane has greater delocalization direction and more ability to split electrons and holes at its surface in presence of lowest wavelength energy 0.05eV (shown in Fig.4). As an interpretation from band gap from DOS, well understanding of such shift suggests either more conducting or visible light catalyst behavior. So this material has now activated for the full day span and not only resemble on the UV illuminating span of the day, according to the DFT method. However the According to H. Hussain et al., a model for a photocatalytic interface between liquid water and rutile TiO_2 for (110) plane has terminal hydroxyls in the contact layer (which obtained from a combination of data from real-space imaging, spectroscopic measurements and surface X-ray diffraction, with interpretation aided by DFT calculations) and its likely open up new reaction pathways to water oxidation [27].

The comparison of Fig.5 with Fig.2 has clearly shown the splitting of states corresponding to the Ti orbitals in to two. Since Ti is d block element and the crystal field for Ti ions makes sense to split these orbitals into t_{2g} and e_g states in the octahedral field of Oxygen. The surface is seemed more metallic in nature since there are small discrepancies in the bandgap of experimental and theoretical TiO_2 due to modeling parameters like exchange correlation pp and Hubbard potential etc. However, the theoretical value in literature seemed less compare to experimental and our Fig.1 TiO_2 shows good agreement with those, we report this prediction of significance of (110) slab is not worthless. In addition to this, for the photocatalytic process if high-temperature treatment synthesized TiO_2 was taken selected then it might generate titanium trivalent (Ti^{3+}) on the TiO_2 particles' surface, which is very reactive [28], [29].

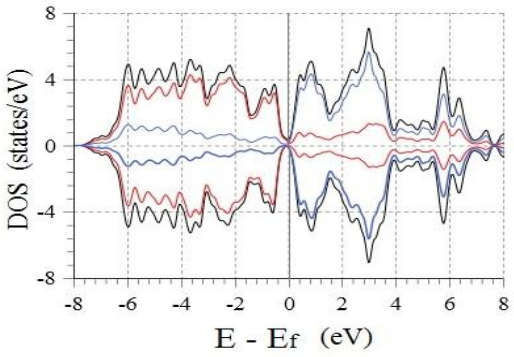

Figure 5: PDOS for (110) slab for the orbital component illustration. Colour indicated as; Blue is Ti (mostly 3d) and Red is O (mostly 2p) orbitals' states.

The predicted (110) surface for better catalyst activity is shown in Fig.6. In the Crystal field of 6 O ligands over the Ti

barycenter in a unit cell illustrated showing pink colour as a (110) plane in first diagram. In second diagram, an arrangement of octahedral single plane (in the z-direction perpendicular to the plane of paper) has illustrated. The predicted surface has illustrated in third diagram. Among the other application the interaction of water with (110) surface has already reported by A. A. Skelton et.al [6] in this regard.

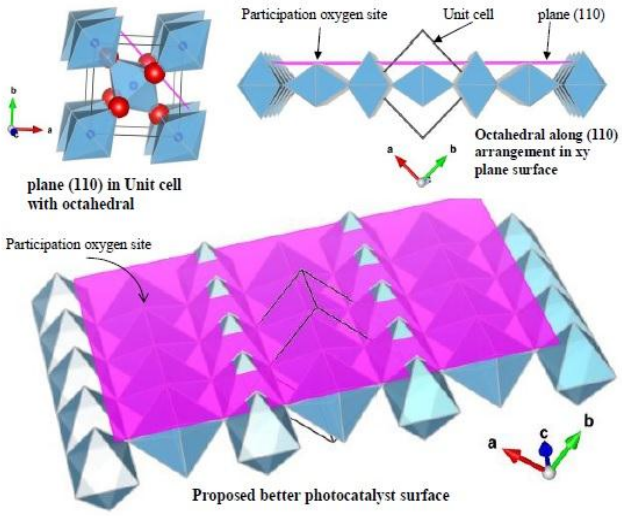

Figure 6: Perspective of the predicted better photocatalyst surface

IV. CONCLUSIONS

From the present theoretical study, we reported that the (110) plane is better with compare to other planes in term of studied property and it is found useful for the photo-catalytic applications as a surface plain on a substrates or in a molecular assembly. It has found prominent for higher wavelengths above the near-UV. TiO_2 (110) seems in-distinguished catalyst here and we suggested it for the photo-catalyst in addition to the bio-compatible, dis-infective and deodorize application. The (110) Millar-cut plane slab surfaces are preferred for these applications and recommended to make such slab surfaces in atmospheric conditions over solid surfaces, porous filters or as suspended particles for the experimentalist and manufacture in this area.

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