Tuning optical properties of TiO₂ by dimension reduction: from 3D bulk to 2D sheets along {001} and {101} plane

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Abstract
The use of two-dimensional sheets exclusively composed of reactive facets of TiO₂ catalyst to explore the possibility of enhanced photocatalytic activity has been an exciting research frontier recently. Using first principles calculations, in this paper we investigate the optical properties of bulk and two-dimensional TiO₂ nanosheets, pointing out to what extent the reduced dimensionality and dimension might enhance the photocatalytic reactivity of TiO₂. The detailed optical properties of 2D sheets of TiO₂ generated along the two distinct facets like (001) and (101) are studied extensively and compared with the bulk counterpart of TiO₂ for electronic and optical properties. The TiO₂ along (101) sheet is found to retain the semiconducting phase whereas the sheet along (001) direction found to be metallic. We found the anisotropy in TiO₂ – 101 to be in four directions while TiO₂ – 001 to be in two directions. Hence their applications as good optical materials are inevitable. Among the two, TiO₂ – 101 sheet shows better absorption coefficient and extinction coefficient indicating better absorbance but TiO₂ – 001 shows better reflectivity in the visible range of solar spectrum. Thus, we report that (001) and (101) nanosheets of TiO₂ differ in their electronic structures and hence in optical properties and so can be used in different photocatalytic and optoelectronic applications well.

1. Introduction
The facet engineering of semiconductor photocatalysts is an interesting and promising area of research and a tool to combat the environmental concerns through better means like alternate fuels and artificial photosynthesis. Semiconductor photocatalysts have long been used in crucial areas such as the deterioration of natural environments created by pollutants, and their role in environmental upkeep have been an area of relentless research [1, 2]. TiO₂ has been a very important oxide semiconductor photocatalyst that has been extensively researched for various applications [3, 4]. Owing to its chemical stability, high chemical inertness, nontoxicity, and low cost, it has been proved to be a universal panacea for many energy applications and controlling of pollutants by degradation [5, 6]. The photocatalytic and photoelectric properties for semiconducting photocatalysts can be well optimized by controlling the growth of their desired crystal facets. In this context the (001) facets of TiO₂ have high photocatalytic activity. Anatase TiO₂ has a truncated bipyramidal shaped tetragonal crystal structure. Its surface is dominated by 94% (101) facets having low surface energy of 0.44 Jm⁻² and 6% (001) facets with surface energy of 0.90 Jm⁻² [7, 8]. Being more photocatalytically active and less thermodynamically stable than (101) facets, (001) facets are known to be the predominant cause for several photocatalytic reactions. Thus far both theoretical calculations and experimental results have ascertained the cause of reactivity of TiO₂ crystals to the more reactive minority (001) surfaces rather than the prominently exposed stable (101) surfaces. Hence it has been extremely attractive and worthwhile to create structures with predominantly (001) facets. Many applications of TiO₂ nanomaterials, however, suggest a strong correlation to their optical properties [9, 10]. TiO₂ nanomaterials normally are usually transparent in the visible light region. Improved optical sensitivity and activity of TiO₂ nanomaterials in the visible light region can be brought about...
by doping or sensitization. Thus, one of the goals for improvement of the performance of nanostructured TiO$_2$ is to increase their optical activity by shifting the onset of the response from the UV to the visible region [11, 12].

Yang et al [7] were the first who succeeded in creating TiO$_2$ structures with 47% of exposed (001) facets by using HF as a capping agent. There has been a great interest to synthesize TiO$_2$ nanosheets of (001) facets and study their enhanced photocatalytic activities [13, 14]. It has been observed that TiO$_2$ nanoparticles exhibit greater photocatalytic efficiency due to reduced recombination rate of e-h pairs. A TiO$_2$ crystallite could have an extremely small thickness of nanometer range and a lateral size ranging from sub micrometers to several tens of micrometers [15]. Thus a nanosheet crystallite is considered to be composed entirely of surface atoms arranged two-dimensionally in a single-crystal-like order. The nanosheet thus may be useful in examining various reactions at the surface and interface level [13]. Hence their unusual structural features are expected to demonstrate novel chemical and physical properties that can differ entirely from those for granular titanium oxides [16]. Luan et al [17] have synthesized new TiO$_2$ nanosheets and found them to be more photocatalytically active in UV region towards degrading methylene blue. They have added graphene oxide (GO) composites into the nanosheet and observed that photocatalytic activity can be optimized by varying the GO content. Han et al [18] have shown that 89% of (001) facets in TiO$_2$ nanosheet showed greater photocatalytic activity. Dette et al [19] have succeeded in creating a new surface phase of anatase (101), which combines two highly desirable attributes, namely a reduced bandgap in the visible region and higher chemical reactivity. This new surface phase lacks the outermost oxygen layer of the stoichiometric surface and is entirely made up of a layer of Ti4c atoms. Sakai et al [16] have studied the nanosheet of TiO$_2$ with 0.7 nm thickness and lateral size ranging from submicron to several micrometers. These nanosheets showed a bandgap of 3.8 eV which was higher than the bulk TiO$_2$ bandgap of 3.2 eV. The higher bandgap of the nanosheet can be attributed to quantum size effects. The first principle calculations of the electronic, optical and other properties of TiO$_2$ nanosheets and comparison to their bulk counterparts have been well studied by Sato et al [20]. The (001) facet dominated catalysis can affect the optical, electronic and photocatalytic properties of nanomaterials due to their morphology. Sajan et al [21] have given a detailed review of the state- of- the-art in (001) facet dominated synthesis of TiO$_2$ nanosheets and their superior properties.

Since the nanosheets of TiO$_2$ show a higher bandgap which falls in the UV region, efforts are on to make the nanosheets photocatalytically active in the visible light [11, 22]. Doping with transition elements etc have not reaped desired results [23]. N doping has given visible light activity to bulk TiO$_2$ [24]. While (001) sheets of TiO$_2$ as such have shown no visible light activity, Liu et al [25] have shown that nitrogen doping causes visible light photocactivity of anatase TiO$_2$ sheets with dominant (001) facets. Using first-principles calculations and optical absorption study, they suggest the band gap narrowing behavior occurs upon nitrogen doping due to shift of the valence band maximum and introduction of some localized states in the band gap. Similarly Maisano et al [26] have shown that 60% of (001) facets on the surface show rather superior photocatalytic activity. Fang et al [27] have studied the superior photocatalytic properties of (001) nanosheets of TiO$_2$. They review the various improved reactions caused by (001) rich and (101) rich facet nanosheets in a comprehensive manner. Xu et al [28] have worked on (100) ultrathin nanosheets of TiO$_2$ having dimensions of 2 nm and 95% exposed (100) facets. They have shown that photocatalytic activity increases many fold due to the increased surface area of the reactive sites.

Not only anatase, rutile TiO$_2$ has also been extensively studied. Hameeuw et al [29] have reported their studies on Rutile (110) surface, how the bridging oxygen vacancies in subsurface enhances their properties, for instance, to molecule adsorption. In another study, Hameeuw et al [30] have studied Rutile (110) surfaces based on three different models of atomic displacements and converged their electronic and geometric properties obtained from DFT calculations with experimental results. Guo et al [31] have reviewed the progress in photocatalytic chemistry of many organic and inorganic molecules on Rutile (110) surface.

Iacomino et al [32] report that DFT studies on anatase nanowires grown in (001) and (010) directions indicate (010) being more crystalline than (001). Also quantum confinements of (001) direction in 1D nanowires enhance their photocatalytic efficiency towards H$_2$ splitting and also are better hydrogen sensors. Vorontsov et al [33] have shown that Anatase (001) quantum dots are evidently visible light photocatalysts inspire of their large bandgap of 3.4 eV. This is attributed to the quantum size effects.

Chido et al [34] have reported how anisotropic spatial distribution of the first allowed optical transitions is related to the crystal structure of the two phases viz, anatase and rutile TiO$_2$. Thus improving the photocatalytic properties in the visible region is still a key challenge. Therefore in this paper we study the optical and dielectric properties of the nanosheets consisting of entirely (101) and (001) facets each based on a computational approach.
2. Computational method

For this project, the calculations have been performed using first principle density functional theory (DFT) within Vienna Ab-initio Simulation Program (VASP) package. The energy cut-off for the plane wave basis set was optimized to be 550 eV. For ground state structure optimization, the Brillouin zone of the supercell was sampled by optimized \(3 \times 3 \times 1\) Monkhorst-Pack K point mesh whereas for electronic structure calculation a higher mesh of \(5 \times 5 \times 1\) was used. For the DOS calculations the Brillouin zone was sampled with a mesh of \(16 \times 16 \times 1\) for TiO\(_2\)–101 sheet, \(24 \times 24 \times 1\) for TiO\(_2\)–001 and \(24 \times 24 \times 24\) for Bulk-TiO\(_2\).

The DFT calculations were performed on a \(2 \times 1 \times 1\) supercell along (101) plane by creating 101-TiO\(_2\) 2D sheet consisting of fourteen Ti and twenty two O atoms (figure 1(b)) and a \(2 \times 2 \times 1\) supercell along (001) plane by generating 001-TiO\(_2\) 2D sheet having twelve Ti atoms and sixteen oxygen atoms as shown in figure 1(c). During simulation the interlayer gap separation between two successive periodic images were kept to be 20 Å so as to avoid the interaction and maintain the 2D confinement. The criterion of electronic convergence in the self-consistent field was \(10^{-7}\) eV and the force convergence was set to be 0.001 eV/Å. The generalized gradient approximation [36] of Perdew–Burke–Ernzerhof (PBE) [37] was used to treat the exchange-correlation energy. Figure 1 gives the structures of the TiO\(_2\) supercells considered for our present study. Further the (101) and the (001) planes are generated from the bulk TiO\(_2\) structure as shown in the shaded region in figure 1(a).

2.1. Optical properties

The optical properties of solids are given by the response of the electron system to a time-dependent electromagnetic perturbation caused by the incoming light. The calculation of these properties is simply the calculation of a response function which is the complex dielectric tensor. The frequency dependent dielectric matrix was calculated using VASP 5.4 optical programs. All the calculations were performed using \(6 \times 6 \times 1\) grid mesh of Monkhorst-Pack scheme for (001) and (101) planes and \(6 \times 6 \times 6\) for bulk TiO\(_2\).

To evaluate optical properties of (001) and (101) nanosheets of TiO\(_2\), the dielectric tensor is calculated following Kubo-Greenwood type formula, where the imaginary part of the dielectric tensor is the sum over occupied and unoccupied bands of the dipole matrix elements, neglecting local field effects [38]. The frequency dependent dielectric matrix is calculated after the electronic ground state has been determined. The dielectric function which is sum of the real and imaginary part can be expressed as,

\[\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)\]

where, \(\varepsilon_1(\omega)\) and \(\varepsilon_2(\omega)\) are the real and imaginary parts of the complex dielectric function.
The imaginary part $\varepsilon_2$, is derived by summing over conduction bands as,

$$
\varepsilon_{2\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q} \sum_{\mathbf{k} \in \mathbf{k}} 2\epsilon_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} - \omega) \langle u_{\mathbf{k}+\mathbf{q}} | u_{\mathbf{k}} \rangle \langle u_{\mathbf{k}+\mathbf{q}} | u_{\mathbf{k}} \rangle^*.
$$

(2)

Here, $c$ and $v$ refer to conduction and valence band. $u_{\mathbf{k}}$ and $u_{\mathbf{k}+\mathbf{q}}$ are the cell periodic parts at k-point $k$, $e$ is the electronic charge. $\Omega$ is the unit cell volume and $\omega$ the plasma frequency. $\epsilon_{\mathbf{k}}$ is the single particle energy. The factor 2 comes from the summation over the spin. The $e_{\mathbf{k}q}$ and $e_{\mathbf{k}q}$ vectors are unit vectors for the three Cartesian directions. $\omega_k$ is weight of $k$-Point vector.

From the imaginary part of the dielectric tensor component the corresponding real part which is obtained from Kramers–Kronig relation can be expressed as,

$$
\varepsilon_{1\alpha\beta}(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_{2\alpha\beta}(\omega')\omega'}{\omega^2 - \omega'^2 + i\eta} d\omega'
$$

(3)

where $P$ is the principal value of the integral.

Then other energy dependent optical parameters can be determined using these obtained values of $\varepsilon_{1}(\omega)$ and $\varepsilon_{2}(\omega)$. The reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, refractive index $\eta(\omega)$, energy loss spectrum $L(\omega)$, and extinction coefficient $\kappa(\omega)$ are evaluated as,

$$
R(\omega) = \left[ \frac{\sqrt{\varepsilon_1(\omega) + j\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1(\omega) + j\varepsilon_2(\omega)} + 1} \right]^2
$$

(4)

$$
\alpha(\omega) = \sqrt{2} \omega \left[ \sqrt{\frac{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}{2}} \right]^2
$$

(5)

$$
\eta(\omega) = \frac{\sqrt{\frac{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}{2}}}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}
$$

(6)

$$
L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}
$$

(7)

$$
\kappa(\omega) = \left[ \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}}{2} \right]^2
$$

(8)

3. Results and discussion

3.1. Structural properties

The optimized structure of bulk TiO$_2$, the two-dimensional (2D) sheets of TiO$_2$ generated along (101) and (001) are depicted in figures 1 (a), (b) and (c) respectively. For the bulk TiO$_2$, the Ti–O bond length, are observed to be 1.93 Å and 1.97 Å. Ti–O–Ti bond angles 97$^\circ$ and 164$^\circ$ and O–Ti–O bond angles ranging from 70$^\circ$–180$^\circ$ respectively agreeing well with the experimentally verified structure of TiO$_2$ [39, 40] and with the report of Iacomino et al [41] where they have mentioned a correlation of the bond lengths with coordination number stating that bond length of Ti–O decreases with increased coordination number of Ti atom. Cromer et al [42] (1955) have reported the Anatase Ti–O bond lengths as 1.937 and 1.964 Å. Mo et al [10] report the O–Ti–O bond angles as 77.7$^\circ$ and 92.6$^\circ$.

In case of 2D TiO$_2$ sheet generated along 101 direction (TiO$_2$–101) the Ti–O bond distances range from 1.8 to 2.12 Å. The Ti–O–Ti bond angles also vary from 90.5$^\circ$ to 175.8$^\circ$, and the O–Ti–O angles range from 80.4$^\circ$ to 139.4$^\circ$. This shows that as Ti–O bond length increases along the (101) plane compared to the bulk structure the bond angle too correspondingly varies considerably distorting the regular tetragonal shape of the bulk. The bond angles are considerably expanded losing the regularity found in the bulk.

In the case of 2D TiO$_2$ sheet generated along 001 (TiO$_2$–001) the optimized Ti–O bond lengths range from 1.91 to 2.17 Å. The Ti–O–Ti angles are in 85$^\circ$ to 96$^\circ$ range and O-Ti-O angles vary from 87$^\circ$ to 174$^\circ$. The O–Ti–O angles are distinctly lower than the bulk depicting the right angled structure of (001) plane. Liu et al [13] have reported that the high-energy (001) facets are typically characterized by higher densities of under-coordinated Ti atoms and have large Ti–O–Ti bond angles compared to that of the bulk. Yang et al [43] have reported the 2D sheets exhibiting remarkable distortion to the T-shaped bonding structure which is formed by O and its three neighboring Ti atoms of the bulk TiO$_2$.

Similar to above, we also observe expansion in Ti–O bond length for the two mentioned planes indicating decrease in coordination number of the Ti atom in the 2D sheets.
3.2. Electronic structure

The density of states of TiO$_2$ in its bulk (B-TiO$_2$) and that of two dimensional sheets TiO$_2$–101 and TiO$_2$–001 are depicted to reveal their corresponding electronic structures in figures 2, 3 and 4 respectively.

The electronic structure of Bulk TiO$_2$ reveals a bandgap opening of 1.5 eV which agrees well with previously reported theoretical work $^{[44]}$. The valence band region is mostly dominated with O-2p states whereas most available states at the conduction band regions are Ti-3d states.

According to Landmann et al $^{[45]}$, deviations from ideal sp$^2$ hybrid states in the DOS for bulk anatase compared to that in rutile are due to the T-like shape of the OTi$_3$ building blocks found in anatase.

The partial density of states (SPDOS) of TiO$_2$–101 and TiO$_2$–001 2D sheets are presented in figures 3 and 4 respectively. The bandgap of TiO$_2$–101 is estimated to be 1.0 eV whereas that of TiO$_2$–001 sheet shows a metallic nature. Though the size reduction in some semiconductors result in a higher bandgap compared to their bulk counterpart experimentally, in case of TiO$_2$ the computational bandgaps are rather different and the smaller gaps in TiO$_2$–101 and TiO$_2$–001 can be attributed to the short coming of our chosen exchange correlation functional. Yang et al $^{[43]}$ have reported DOS and PDOS for (001) and (101) sheets for rather smaller supercells.

**Figure 2.** The partial density of states of Bulk TiO$_2$. Pink Dotted line presents the Fermi Level.

**Figure 3.** The partial density of states of 2D TiO$_2$–101 sheet. Pink Dotted line presents the Fermi Level.
On the basis of the XPS valence band spectra and DFT calculations, the DOS plots by Liu et al\[46\] state depicts a smaller bandgap for the (001) face than (101) face and the VB maximum of (101) remains same as that of (001), whereas, the CB minimum of (101) is higher. In general, in case of 2D sheets, very few states are available near the Fermi level when compared to the density of states of their bulk counterpart. For (101) 2D structure the band gap regions are populated with very few Ti-3d states which could be due to PBE exchange functional and can further be verified with more intense hybrid functional calculations. The calculated surface energies of TiO$_2$–101 and TiO$_2$–001 sheets are reported in literature to be 0.44 and 0.90 Jm$^{-2}$ respectively\[13, 47, 48\] and it is evident that TiO$_2$–101 is more stable than the corresponding (001) plane. This is due to the Ti atoms in (101) plane having reduced coordination number than that in (001) plane as shown in figure 1. Liu et al\[13\] have reported unique geometrical and electronic properties of (001) facets favoring dissociative adsorption and spatial separation of the redox sites. The facets-mediated behavior in adsorption and charge transfer accounts for the superior photo reactivity of TiO$_2$ sheet along (001)-face compared to that of (101) face.

### 3.3. Dielectric and optical properties

The optical properties of the solid are governed by the interaction between the solid and the electric field of the electromagnetic wave. In this section the dielectric function as well as optical properties of B-TiO$_2$ structure is compared with those of TiO$_2$–001 and TiO$_2$–101 2D sheets.

#### 3.3.1. Dielectric Function

Figure 5 represents the Imaginary parts of Dielectric function for all three cases of TiO$_2$ and figure 6 represents the corresponding Real parts of the Dielectric function.

The imaginary part for the B-TiO$_2$ is shown from 1–7 eV range, whereas those of TiO$_2$–001 and TiO$_2$–101 are prominent in the range of 0–5 eV. B-TiO$_2$ shows two intense peaks along both yy, zz directions at 7 eV and 4 eV and in the range 4–10 eV in xx direction. The spectral shape of polarizations along different axis is in very good agreement with previously reported results. Both along x and y direction, the peak onsets from 2 eV upto 5 eV and along the z polarization the intense peaks (excitonic) at 3 eV and 4 eV resemble well to the peaks of the work reported by Chiodo et al\[49\]. The imaginary part also shows resemblance to the earlier work of Mo et al\[10\].

The static dielectric constant is obtained from $\varepsilon_1(\omega)$ in the zero frequency limit [50–52]. From the real parts of dielectric function plots in figure 6, dielectric constants are 6.8, 8 and 7.6 for the B-TiO$_2$ agreeing well with previously reported literature values [53]. For the TiO$_2$–001 plane, we see that static dielectric function is 5.9. For the TiO$_2$–101 plane, dielectric function values vary in all four directions. Along xx and zx direction, the dielectric constants are depicted at 4.6 in xx, 5.28 in yy, 4.2 in zz and 1.01 in xz directions. The anisotropy differs in all four directions for the TiO$_2$–101 plane while for TiO$_2$–001 planes they are unique in zz direction. Since anisotropy is higher in all directions for (101) plane, we can understand that (101) sheet can be a better material for
optoelectronic applications. Moreover, as coordination number reduces from bulk to sheet, their static
dielectric constants decrease significantly. The ions are denser and coordination number is higher in the bulk
compared to sheets as indicated by higher dielectric constants for the bulk [54].

3.3.2. Absorption coefficient
Figure 7 gives the absorption coefficients of the TiO$_2$ bulk and sheets. The B-TiO$_2$ shows a high absorbance
where peaks along xx, yy and zz are $2.8 \times 10^5$, $2.6 \times 10^5$ and $3.4 \times 10^5$ cm$^{-1}$ in the energy range of 5–10 eV and
then in the range of 20–25 eV. For TiO$_2$–001 plane, the absorbance for directions xx and yy is $0.96 \times 10^5$ cm$^{-1}$
and zz is $1.4 \times 10^5$ cm$^{-1}$, with prominent absorption peaks in the 8.6 eV region. For TiO$_2$–101 plane the
absorbance peaks are in the range $0.57–1.13 \times 10^5$ cm$^{-1}$ all occurring predominantly between 9.5 and 5.5 eV.
The absorbance for the B-TiO$_2$ is highest with $3.4 \times 10^5$ cm$^{-1}$ while absorbance is around $1.1 \times 10^5$ cm$^{-1}$ for
As absorbance is inversely related to the absorption length, it follows that absorption length for B-TiO$_2$ is lowest. Similarly the photon energies for absorption of TiO$_2$–101 sheet are lower than TiO$_2$–001 sheet. Hence TiO$_2$–101 shows the superior optical properties even at smaller thickness because of its better absorptive power at lower energies.

Here, in case of both the studied sheets, enhancement of photocatalytic activity is observed in visible region. The absorbance is shifted more to lower energy region for both the 2D sheets compared to that of the bulk counterpart. However Liu et al have reported only appreciable visible-light reactivity for pristine anatase TiO$_2$ along (001) facets as well as for doped TiO$_2$ sheets.

### 3.3.3. Electron energy loss spectrum (EELS)

The energy-loss spectrum (EELS) in figure 8 describes the energy loss of a fast electron traversing in the material. For B-TiO$_2$, Plasmon peaks are found for zz at 30.6 eV and the less intense peaks along xx, yy directions are observed at 30.4 eV which correspond to the free electron Plasmon peak. In this context, Mo et al [10] have reported Plasmon peak at 12.5 eV for bulk anatase in 0–20 eV range which is similar to the peak appearing in the 12 eV range in our work. The Plasmon peaks represent the energy of collective excitations of the electronic charge density in the crystal. For the bulk, EELS increases in the range from 5 eV up to 30 eV after which it rather decreases.

For TiO$_2$–001, the Plasmon peaks for both (xx, yy) and zz are located between 9.8–10.2 eV. For TiO$_2$–101, all the Plasmon peaks for three directions are seen in the range 9.2 to 9.8 eV. The intensity decreases very sharply with increasing loss energies and shows step-like structure corresponding to the ionization threshold energies $E_i$ of core level electrons.

The inter band transitions are from 4–36 eV for B-TiO$_2$. The Plasmon peaks of the valence electrons are found in 30 eV region for B-TiO$_2$. However the Plasmon peaks are near 10 eV for TiO$_2$–101 sheet with interband transitions up to 25 eV and that of the TiO$_2$–001 sheet is found at 10 eV and interband transitions on either side extending up to 20 eV. Since the Plasmon peaks decrease in intensities from B-TiO$_2$ to TiO$_2$–001 to TiO$_2$–101, the sheet structures are predicted to be more dense or crystalline compared to their bulk counterpart [56] which is also in agreement with Hengere et al [57] as they have reported that TiO$_2$ is less dense and more open along the (001) planes as compared to the (101) planes.

### 3.3.4. Extinction coefficient

The extinction coefficients for the bulk and sheets of TiO$_2$ are shown in figure 9. The B-TiO$_2$ show values of 1.8, 2.6 and 2.8 for xx, yy and zz directions in the energy range from 4–12 eV. For the TiO$_2$–001 sheet, the extinction coefficients of 9.51 and 1.72 are highest at 0.2 eV and 2.5 eV respectively. For the TiO$_2$–101 case, we see extinction coefficient values of 0.8 to 2.03 in the energy range of 0.2 to 2.2 eV. The extinction coefficients are highest for TiO$_2$–001 which implies it is least absorbing or the decay of light could be faster through TiO$_2$–001.
sheet. The TiO$_2$–001 has better extinction coefficient of 9.51 may be due to its metallic character. Thus it could be the better reflective material of the three cases.

3.3.5. Reflectivity

Figure 10 shows the reflectivity of the three cases of TiO$_2$. The reflectivity of B-TiO$_2$ ranges from 0.2–1 in the four directions and has significant reflectivity which increases up to 10 eV. According to Tang et al [58], the reflectance of Bulk TiO$_2$ has a strong broad structure comprising of three resolvable features at 3.8 eV, 4.2 eV, and 4.7 eV respectively. These dominating peaks correspond to direct allowed interband transitions at critical points. The reflectivity of TiO$_2$–001 sheet is at 0.8 and 0.3 along the two anisotropic directions. The reflectivity range is significant from 0–10 eV for the TiO$_2$–001 sheet. The reflectivity for TiO$_2$–101 plane shows different values in four directions ranging from 0.15 to 1. The reflectivity range is significant from 0–10 eV for the TiO$_2$–101 sheet. The decrease in reflectivity plots correspond to the peaks in Energy loss spectrum for each structure. The reflectivity is higher in the UV-visible region (<6eV) compared to the 5–20 eV range in all three cases. Hence, the structures are reflective in the lower energy region compared to higher energy regions. Among the 2D sheets, TiO$_2$–001 can prove to be a better reflective material owing to its higher values. Groh et al [59] have reported very low reflectivity (<0.09) of BeO$_2$ in the 0–5eV range indicating its utility as a transparent material.

3.3.6. Refractive index

Figure 11 depicts the refractive indices for the three cases of TiO$_2$ under study. For the bulk TiO$_2$, the static refractive indices range from 3.3–3.8 in all the three directions. For the TiO$_2$–001 plane the static refractive indices along xx, yy and zz are 20.39 and 2.8 respectively. For the TiO$_2$–101 plane, four values are seen ranging from 1.2 to 5.06. The TiO$_2$–001 sheet predicts higher refractive index along yy direction compared to other two directions which could be attributed to the higher thickness of the sheet along the yy direction which is supported by already reported results indicating that the increase in crystal size as well as increase in film thickness plays a key role in enhanced refractive index [60, 61]. With enhanced optical properties, both (001) and (101) sheets are predicted to be appropriate to be utilized for optoelectronic applications. All the above optical and dielectric properties have been summarized in table 1 below.

4. Summary

This work gives comparative studies between the electronic and optical properties of bulk TiO$_2$, the 2D sheets generated along (001) facets as well as (101) facets of TiO$_2$. The electronic structures explain the change in hybridization and bonding properties near the Fermi level. The TiO$_2$–101 plane shows a bandgap of ~1 eV and the (001) sheet shows a metallic state whereas bulk TiO$_2$ shows a bandgap of 1.5 eV. While comparing the
complex dielectric functions and optical properties of TiO$_2$–001 and TiO$_2$–101 with that of B-TiO$_2$, the optical anisotropy is evident in both the sheets. The TiO$_2$–101 having relatively greater anisotropy makes it a useful optical material. The optical properties and dielectric constants definitely point to possible enhancement of the visible light activity in the cases of TiO$_2$–001 and TiO$_2$–101 nanosheet compared to their bulk counterpart. The TiO$_2$–001 shows anisotropy in the directions as $\varepsilon_{xx} = \varepsilon_{yy} \neq \varepsilon_{zz}$. However for the TiO$_2$–101, the anisotropy is increased and the dielectric constants and optical properties are different for all four directions, i.e. $\varepsilon_{xx} \neq \varepsilon_{yy} \neq \varepsilon_{zz} \neq \varepsilon_{xz}$. Hence the two sheets can be better alternatives in optoelectronic applications. The reflectivity and extinction coefficient values indicate TiO$_2$–001 could be used as a better reflective material. The extinction coefficient and absorption coefficient for TiO$_2$–101 indicate their better absorption properties.

Figure 9. Extinction Coefficient for the bulk TiO$_2$, TiO$_2$–001 sheet and TiO$_2$–101 sheet.

Figure 10. Reflectivity for bulk TiO$_2$, TiO$_2$–001 sheet and TiO$_2$–101 sheet.
Figure 11. Refractive Index for the bulk TiO$_2$, TiO$_2$–001 sheet and TiO$_2$–101 sheet.

Table 1. Optical and dielectric constant components in four principal directions of bulk, (001) and (101) structures of TiO$_2$ obtained using PBE.

| TiO$_2$ Direction | Dielectric constant $\varepsilon$ | Absorbance ($\times 10^5$ cm$^{-1}$) | Reflectivity (static) | Refraction (static) | EELS Extinction coefficient |
|------------------|-------------------------------|----------------------------------|---------------------|-------------------|--------------------------|
| Bulk             | xx                            | 6.8                              | 2.89                | 2.0               | 3.3                      | 2.2                      | 1.8                      |
|                  | yy                            | 8                                | 3.0                | 1.3               | 3.6                      | 2.5                      | 2.6                      |
|                  | zz                            | 7.6                              | 3.4                | 0.8               | 3.8                      | 3.2                      | 2.8                      |
|                  | xz                            | 0                                | 0.96               | 0                 | 0                        |                          |                          |
| 001              | xx                            | —                                | 0.964              | 0.8               | 20.39                    | 1.316                    | 9.51                     |
|                  | yy                            | —                                | 0.964              | 0.8               | 20.39                    | 1.316                    | 9.51                     |
|                  | zz                            | 5.9                              | 1.40               | 0.37              | 2.821                    | 2.006                    | 1.724                    |
| 101              | xx                            | 4.6                              | 1.06               | 0.4               | 5.06                     | 1.78                     | 2.037                    |
|                  | yy                            | 5.28                             | 1.13               | 0.28              | 3.196                    | 1.467                    | 1.328                    |
|                  | zz                            | 4.2                              | 0.95               | 0.15              | 2.18                     | 1.355                    | 0.8157                   |
|                  | xz                            | 1.01                             | 0.567              | 1                 | 1.27                     | —                        | 0.967                    |

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