Amorphous TiO$_2$ as a photocatalyst for hydrogen production: a DFT study of structural and electronic properties

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Abstract

In recent years, photocatalytic splitting of water to produce hydrogen has attracted significant attention. Crystalline forms of titanium dioxide (TiO$_2$) have been investigated for decades. Amorphous TiO$_2$, although less expensive, has not been studied as thoroughly. This study investigates the structural and electronic properties of amorphous TiO$_2$. Molecular dynamics simulations are used to prepare multiple amorphous TiO$_2$ samples having different number of atoms. The structural analysis agrees well with the experimental data. Electronic properties of amorphous TiO$_2$ are investigated through density functional theory calculations. Band gap characteristics of amorphous TiO$_2$ are compared with experimental data for amorphous as well as crystalline (rutile and anatase) TiO$_2$ phases. Analysis of electronic properties suggests that amorphous TiO$_2$ may prove as a cheaper, more abundant, but somewhat less efficient photocatalyst as compared to crystalline TiO$_2$.

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Keywords: Hydrogen production; Photocatalysis; Amorphous TiO$_2$; Structural properties; Electronic properties.

1. Introduction

Titanium dioxide (TiO$_2$) is a safe, abundant and inexpensive photocatalytic material. It has therefore attracted wide attention in recent years for photocatalytic splitting of water [1-3], water decontamination [4] and solar cells [5, 6]. Most of the efforts so far have been focused on improving the photocatalytic properties of the crystalline phases only, as the amorphous TiO$_2$ structure is reported not as good photoactive substance due to its broad band gap and disorder [7]. However, amorphous TiO$_2$ (aTiO$_2$) has a larger surface area which leads to higher adsorptivity. It is also more widely available in nature and can be prepared at room temperature. Furthermore, it is easier to process into different forms and may allow...
much wider range of dopants. These useful characteristics have led to recent attention to exploring aTiO$_2$ as an alternative to crystalline TiO$_2$ phases. Quite recently, aTiO$_2$ dye sensitized solar cell has been found to exhibit higher efficiency as compared to the nano-crystalline TiO$_2$ layer [8]. Buddee et al. [9] have reported that Fe/Cr doped aTiO$_2$ showed enhanced photocatalytic activity under both UV & visible light and these can also be used endlessly without any changes, indicating another significant advantage of aTiO$_2$ over crystalline forms. More recently, Chen et al. [10] have prepared disorder engineered TiO$_2$ nanocrystals and found that mid gap states arising out of structural disorder upshift the valence band edge effectively reducing the band gap and increasing its photocatalytic efficiency.

In view of above reports, it is therefore necessary to understand the atomic level structure of aTiO$_2$, its electronic properties in more depth; and explore its potential as a cost-effective photocatalyst for large-scale hydrogen production through sunlight-enabled water splitting. In this study we analyze the structural disorder and electronic properties of aTiO$_2$ in detail through density functional theory (DFT) calculations. The defects in aTiO$_2$ and the localized states in the band gap corresponding to the structural defects are identified. As amorphous semi-conductors are difficult to model due to lack of periodicity and the complexity of structural details at the atomistic level, we propose atomistic aTiO$_2$ models formed by molecular dynamics (MD). Multiple aTiO$_2$ samples having different number of atoms and using different heating and quenching rates are also investigated. To confirm the amorphicity of the models, structural properties are compared to experimental data. Finally, the electronic properties of aTiO$_2$ are calculated using DFT and compared with the crystalline phases.

2.  Computational details

2.1 Sample preparation methodology

Three model samples of bulk aTiO$_2$ with supercell dimensions of $2 \times 2 \times 3$ (72 atoms); $2 \times 2 \times 4$ (96 atoms) and $3 \times 3 \times 4$ (216 atoms) were prepared using Molecular dynamics (MD) simulations. Initial configuration of three samples having cubic supercell was chosen with a side length obtained by rescaling crystalline configuration of rutile (tetragonal, space group p42/mnm) so as to have density equal to aTiO$_2$, i.e. 3.8 g cm$^{-3}$, with lattice parameters $a = b = 4.761$ Å, $c = 3.066$ Å and $\alpha = 0.305$. Matsui-Akaogi (MA) force field [11] was used for calculating short range interactions; and the affect of long range Coulomb interactions were taken into account using damped shifted force Coulomb sum method. MD simulations were carried out using DLPOLY [12]. Periodic boundary conditions were used. Each sample was first subjected to geometric optimization in micro canonical ensemble (NVE) by ‘zero’ temperature MD. To eliminate the memory of initial structure, all the crystalline samples were first heated up to temperature greater than the melting point of rutile, as performed by Rino et. al [13]. Thereafter the sequential heating and quenching were performed. After every heating and quenching, samples were equilibrated for sufficiently long time to assure that they attain the steady state configurations, with a simulation time step of 1 fs. After quenching the samples to the room temperature followed by equilibration, they were finally relaxed to 0 K to attain ground state.

The above sample preparation process can sometimes lead to dangling bonds which can cause erroneous band gap levels, see e.g. [14]. Therefore, careful checks were performed periodically to make sure that no atom should remain unbonded creating dangling bonds. The structures of prepared samples are presented in Figs. 1 (a), (b) and (c) respectively. Final samples obtained from MD at 0K temperature were further relaxed using DFT calculations before calculating there structural and electronic properties. Details of the ab-initio calculations are provided below.
2.2 Ab-initio calculations of electronic properties

DFT calculations were performed using Quantum Espresso [15] software package to investigate the electronic characteristics of aTiO$_2$ samples. The interaction between the valence electrons and the ionic core is described by the generalized gradient approximation (GGA) in the Perdew-Burke-Erzerhof (PBE) formulation [16] and Vanderbilt ultrasoft pseudo-potentials [17]. The wave functions were expanded with kinetic energy cutoffs of 40 Ry and 400 Ry for the smooth part of the electronic wave functions and augmented electron density, respectively. The Monkhorst-Pack grid [18] with $2 \times 2 \times 3$, $2 \times 2 \times 3$ and $1 \times 1 \times 2$ k points was used in SCF iterations and $4 \times 4 \times 6$, $4 \times 4 \times 6$ and $2 \times 2 \times 4$ k points was used for electronic density of states (DOS) computation for 72-atom, 96-atom and 216-atom model respectively. These values were chosen after full convergence studies. All calculations were spin polarized. The atomic structures were relaxed using the conjugate gradient minimization algorithm, until the magnitude of residual Hellman-Feynman force on each atom was less than $10^{-3}$ Ry/Bohr. Before electronic properties calculations all the samples were relaxed at zero pressure by variable cell relaxation. In order to enable direct comparison of amorphous TiO$_2$ with crystalline phases, rutile and anatase structures were also investigated. The bulk lattice parameters for zero pressure crystalline TiO$_2$ obtained by variable cell relaxation using DFT were in reasonable agreement with experimental data. For instance, the lattice parameters for rutile obtained in this calculation are $a = b = 4.6155$ Å and $c = 2.96$ Å which agree with experiments [19-22] as well as with theoretical calculations [23-26].

3. Results and discussion

3.1 Structural Properties

Before calculating electronic properties of amorphous samples, their structural properties were calculated and compared with experimental data to ensure the amorphicity of the model aTiO$_2$ samples. Specifically, partial pair correlation functions (PPCFs), coordination numbers (CNs), bond length, bond angle and dihedral angle distributions were studied. Two-body correlations were determined by PPCF, $g_{\alpha \beta}(r)$, which is defined as

$$\langle n_{\alpha \beta}(r) \rangle \Delta r = 4\pi r^2 \rho \rho_{\beta} g_{\alpha \beta}(r) \Delta r$$

(1)

where $\langle n_{\alpha \beta}(r) \rangle \Delta r$ is the number of $\beta$ particles in the shell of inner radii $r$ and thickness $\Delta r$, around particle $\alpha$. The angular brackets denote the ensemble average as well as the average over all the $\alpha$'s. The
number density $\rho = N/\Omega$, with $N = N_{Ti} + N_{O}$ and $\Omega$ is the volume of the system, $c_\beta = N_\beta/N$ is the concentration of $\beta$ particles and $N_\beta$ is their total number. The calculated PPCFs for Ti-Ti, Ti-O and O-O pairs for the three aTiO$_2$ models along with experimental data [27] are shown in Figs. 2. The calculated PPCFs agree reasonably well with experimental data for sputtered TiO$_2$ amorphous layers [27], and as expected, the larger samples correlate better with the reported experimental data. The peak positions in the figure correspond to the nearest neighbour (NN) distances, and are calculated as 3.1 Å and 3.4 Å for the 72-atom model, 3.0 Å and 3.6 Å for the 96-atom model and 3.13 Å and 3.53 Å for the 216-atom model. They are also in close agreement with experiments reported by Petkov et al. [27], who found 1$^{\text{st}}$ and 2$^{\text{nd}}$ nearest neighbor peaks corresponding to edge-sharing and corner-sharing Ti-Ti pairs at 3.0 Å and 3.55 Å, respectively. The calculated Ti-O and O-O 1$^{\text{st}}$ NN distances are at 1.9 Å and 2.8 Å for 72-atom model, 1.9 Å and 2.7 Å for 96-atom model and 1.92 Å and 2.7 Å for 216-atom model, also in reasonable agreement with the experimental values of 1.96 Å and 2.67 Å respectively.

The distribution of coordination numbers (CNs) $Z_{Ti-O}$ of Ti and $Z_{O-Ti}$ of O atoms were determined by counting the number of O and Ti atoms respectively, within the range of first minima of $g_{Ti-O}(r)$ throughout the sample. This minima is found to be 2.85 Å for 72-atom, 96-atom and 216-atom aTiO$_2$ models. CN of Ti is 6 and O is 3 for crystalline bulk rutile but for amorphous TiO$_2$ samples Ti atoms have the CNs 1, 2, 3, 4 and 5 in addition to 6 and O atoms have CNs 1, 2, 4 and 5 in addition to 3. The relative percentages of CNs for amorphous phase are tabulated in Table 1. The average CN of Ti is 4.125, 4.406 and 4.736 for 72-atom, 96-atom model and 216-atom models, respectively. On the other hand, the average CN of O is 2.104, 2.625 and 2.632 for 72-atom, 96-atom model and 216-atom models, respectively. The corresponding experimental CNs for Ti and O are 5.6±10% and 2.8±10% respectively [27]. Above analysis shows that CN of all aTiO$_2$ samples is in agreement with the experimental data. It can be noted from table 1 that most of the Ti and O atoms of amorphous samples tend to remain 6-fold and 3-fold respectively. The larger 216-atom model behaves more like a bulk system and hence agrees more closely with experimental results [27], which were also for the bulk amorphous system.
Table 1: Relative percentages of Ti and O atoms with coordination numbers (CNs) $Z_{Ti-O} = 1, 2, 3, 4, 5,$ and $Z_{O-Ti} = 1, 2, 3, 4$ and 5 for amorphous TiO$_2$ models.

<table>
<thead>
<tr>
<th>CN</th>
<th>72-atom model</th>
<th>96-atom model</th>
<th>216-atom model</th>
</tr>
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<tbody>
<tr>
<td>$Z_{Ti-O}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.17</td>
<td>3.13</td>
<td>2.78</td>
</tr>
<tr>
<td>2</td>
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<td>8.33</td>
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<td>25.00</td>
<td>21.88</td>
<td>12.50</td>
</tr>
<tr>
<td>4</td>
<td>8.33</td>
<td>28.13</td>
<td>12.50</td>
</tr>
<tr>
<td>5</td>
<td>25.00</td>
<td>9.38</td>
<td>20.83</td>
</tr>
<tr>
<td>6</td>
<td>25.83</td>
<td>34.38</td>
<td>40.28</td>
</tr>
<tr>
<td>$Z_{O-Ti}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>10.42</td>
<td>12.50</td>
<td>12.50</td>
</tr>
<tr>
<td>2</td>
<td>62.50</td>
<td>10.94</td>
<td>18.056</td>
</tr>
<tr>
<td>3</td>
<td>14.58</td>
<td>65.63</td>
<td>56.25</td>
</tr>
<tr>
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<td>0.00</td>
<td>7.81</td>
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</tr>
<tr>
<td>5</td>
<td>6.25</td>
<td>0.00</td>
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</tr>
</tbody>
</table>

The analysis of bond length distribution for amorphous models shows that most of Ti-O bond lengths get distributed between 1.86 to 2.1 Å for all the three amorphous samples, whereas for crystalline rutile Ti-O bond lengths are at 2.017 and 2.05 Å. Our results agree well with experimental results of Manzini et al. [28], who found two Ti-O separations of 1.79 and 1.93 Å in amorphous sol-gel TiO$_2$. It is noted that large number of Ti-O bonds get compressed and few get expanded as compared to crystalline phase of TiO$_2$. Bond angle analysis of the amorphous models shows that in the amorphous phase bond angles get dispersed from 55° to 157° although majority of bond angles are between 70° to 110°. Rino et al. [13] also found the main peak at 90°. The dihedral angles in all the amorphous models show no peaked structure and are nearly uniformly distributed between 0° and 360°. Thus, expectedly the planar orientation becomes nearly random for amorphous samples.

3.2 Electronic properties

To describe the electronic structure of amorphous TiO$_2$ the electronic density of states (DOS) and the inverse participation ratio (IPR) were analyzed. The total DOS for all the three model of aTiO$_2$ along with that crystalline rutile of supercell size 2×2×3 (72 atoms) and anatase of supercell size 2×2×2 (48 atoms) using DFT are shown in Fig. 3. To understand the electronic properties in further detail the atomic partial density of states (PDOS) for the d electrons of Ti atom and p electrons of O atoms were investigated for all the samples. As DOS of all the amorphous models have similar characters with slight differences in detail, we have shown PDOS for the 96-atom model only (see Fig. 4). Only the valence band (VB) and conduction band (CB) are shown in the figures. The spin-up and spin-down contributions are displayed as top and bottom, respectively, in Fig. 4. The zero energy value is set at the top of the valence band to analyze the relative change in the band with more clarity. The Fermi energy is represented by the vertical line in the band gap. DOS and PDOS graphs show that VB and CB mainly consists of O p and Ti d orbitals respectively. Thus, high localization obtained in VB and CB tails (shown by IPR analysis, Fig. 5) is on O p and Ti d orbitals respectively. The band gap is measured as difference between highest and lowest occupied molecular orbitals (HOMO-LUMO gap) based on the Γ point in the k-space, as is usually done for crystalline systems. To further understand CB and VB tails, detailed IPR analysis is performed.
The band gap of amorphous models can also be determined by analyzing the change of the localization degree of the electronic states near the VB and CB edges. The localization of each electronic state was quantified here by analyzing the inverse participation ratio in aTiO2. The IPR of an orbital \( \psi_n(\mathbf{r}_i) \), \( I(\psi_n) \), is defined as

\[
I(\psi_n) = N \frac{\sum_{i=1}^{N} |\psi_n(\mathbf{r}_i)|^4}{[\sum_{i=1}^{N} |\psi_n(\mathbf{r}_i)|^2]^2}
\]

(2)

where \( N \) is the number of volume elements in the cell and \( i \) is the index of the volume element. The IPR is large for highly localized states and small for delocalized states. Ideally, a localized orbital presents
\( I(\psi) = N \), whereas a delocalized orbital presents \( I(\psi) = 1 \). Thus IPR can identify a level as belonging to the band (delocalized), to the band tail (partially localized), or to the band gap (highly localized).

The plot of IPR and total DOS for the 96-atom aTiO\(_2\) model is depicted in Fig. 5. The bottom of the CB and the top of the VB was determined as the energy where the IPR becomes higher than the average IPR of those levels sitting a few electron volts below the VB top. The mobility gap, defined as the gap between extended valence and conduction states, is estimated as \( E_g = 2.85 \text{ eV} \) for the 72-atom and 96-atom model and 2.7 eV for the 216-atom model. As a comparison with crystalline TiO\(_2\), we obtained a band gap of 1.78 eV for rutile and 2.53 eV for anatase TiO\(_2\). Experimental values of band gap for rutile and anatase are 3.03 eV [21] and 3.20 eV [35], respectively. Relatively larger band gap of aTiO\(_2\) with respect to rutile and anatase, and the presence of band tail states suggest that it is photocatalytically less efficient than the crystalline forms. Since there is a large number of levels with different IPR’s in the top of the VB, there is some uncertainty in defining the gap. Also as the dimensions of simulation cells considered here are small relative to the bulk amorphous material, the results are expected to improve with increasing model sizes. Finally, it is noted that we used finite cells with periodic boundary conditions. Hence, it is possible that the levels which are in the band tails near the energy-band edges may present some fictitious delocalization. A more detailed investigation on the band tail properties of aTiO\(_2\) with very large simulation cells of a few thousand atoms [36] should be carried out in future studies.

4. Summary

In summary, we have used density function theory to investigate structural and electronic properties of amorphous TiO\(_2\) for use in hydrogen production using photocatalytic water splitting technique. Two body interatomic potential was used to generate three amorphous TiO\(_2\) samples having different number of atoms by “melt-and-quench” method. The structural analysis agrees with the experimental results and hence confirms the amorphicity of the samples. Band gap of amorphous TiO\(_2\) are compared with experimental band gap of amorphous as well as crystalline (rutile and anatase) TiO\(_2\). The spatial localization of all the energy levels has been identified by analyzing inverse participation ratio. From IPR analysis it is found that band tail states near the band edges are localized in amorphous TiO\(_2\) in contrast to the crystalline TiO\(_2\) due to bond angle disorder present. The valence and conduction tail states result from the positional disorder of O and Ti atoms, respectively. The extent of tailing depends on disorder present. Higher is the disorder, more is the overlapping of bands in band gap. The electronic density of states and electronic localization, are quite insensitive to the variation in local disorder among models. The analysis of the electronic properties suggests that the electronic structure of aTiO\(_2\) is similar to that of crystalline electronic structure. Thus, amorphous TiO\(_2\) may prove as a cheaper and more abundant alternative to crystalline forms. However, to fully utilize the potential of aTiO2 as a cost-effective photocatalyst, more detailed investigation on band tails, using larger simulation cells, and doping with suitable elements need to be investigated. These in-depth studies on the role of disorder on electronic properties of aTiO\(_2\) are currently being carried out and will be reported in future.

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