ABSTRACT

Various solar cell architectures and materials are currently studied, seeking enhanced photon management mechanisms. Herein, we provide an attempt to prepare, characterize, model, and simulate a novel semiconductor, Lithium Titanate, which has a band gap of 3.55 eV. The semiconductor was prepared from H₂TiO₃ and LiCO₃ by calcination at 500 °C for 5 h after grinding with deionized water. XRD, SEM, EDX, and AFM carried out a complete morphological characterization on powder and thin-film levels. Additionally, experimentally validated atomistic DFT modeling was performed where the density of states and the imaginary part of the permittivity were extracted. Finally, the optical transmission spectrum was simulated for a 4.28 μm thickness film, with the aid of a finite-difference time-domain solver, against an experimentally measured spectrum, showing a root-mean-square mismatching error of 3.78%.

1 Introduction

With the ever-increasing energy demand [1], continuous research is needed to convert solar energy into usable electrical energy efficiently [2, 3]. Photovoltaic technologies have been desirable for directly converting energy using solar radiation to be converted into electrical energy [4]. Continuous research is carried out to discover more materials that may aid the process and increase the efficient extraction of photons’ energy [5]. One of the significant areas of study is the Dye-Sensitized Solar Cells (DSSCs) [6] and the Perovskites Solar Cells (PSCs) [7]. Both have been intensely studied over the previous years [8–14]. DSSCs have shown an initial high rate of improvement, reaching up to 14% using some inorganic dye as sensitizers [15, 16], while PSCs have tackled the 25% border to be compared with silicon-based cells [17].

Principally, photovoltaics work based on the excitement of semiconductor valence electrons by incident photon energy. This only happens when the
semiconductor's band gap allows for the absorption of the electron. High band gaps pose a challenge in gaining enough energy, while low band gap allows for the re-stabilization of the electrons easily into the valence band, not allowing for the free movement of electrons in the conduction band. This is known as recombination [18]. Mainly, DSSCs work based on sensitization by photons absorbing dye due to coloration, which would assist an oxide semiconductor in achieving an excited state [8]. This would then be passed through the transparent electrodes across the external circuit and back to the cell at the other transparent electrode. The cell would then use the electrolyte to regenerate the semiconductor to keep the process going [8].

For the sake of optimum DSSC Incident-Photon-to-Current Efficiency (IPCE), various catalysts have been investigated in the literature. Nano-rod electrodes structure of hematite for water showed 8% IPCE at \( \lambda = 350 \text{ nm} \), and an intensity of 0.1 mW cm\(^{-2} \), while still high recommendation rates were reported [19]. Bismuth Vanadium tetraoxide electrodes were used the studied for the same purpose and demonstrated an IPCE of 29% in visible light [20]. In addition, it was reported that the proposed semiconductor has a longer lifetime for the photogenerated carrier, which makes it superior to weak semiconductors such as Fe\(_2\)O\(_3\). However, the overall efficiency was only 0.7% [21]. Another attempt to synthesize an efficient photocatalyst for water splitting, lithium titanate (LTO), was studied [22]. The results have shown promising properties for lithium titanate as a photocatalyst and oxide electrode [23].

Another optimization track for DSSC performance is toward the band-gap management of the mesoporous TiO\(_2\) to attract visible photons. This is usually done through doping [12, 14]. Our previous investigation in [14] presented an attempt to narrow the TiO\(_2\) band gap from 3.2 eV to around 2.6 eV with AgVO\(_3\) doping. Herein, doped TiO\(_2\) manages the visible photons absorption process along with the visible dye. However, the main drawback of such architecture is the UV absorptions which deteriorate the cell performance with a significant impact on cell sustainability [24].

Accordingly, we propose the utilization of lithium titanate as a UV absorber in DSSC in the form of a photo-anode layer. Lithium titanate is chosen not only for its band-gap compatibility, around 3.55 eV but also for the simplicity of the fabrication and the deposition process and the adaptability with the TiO\(_2\) layer as a supporting substrate [22]. The current study has demonstrated a new recipe in preparing the proposed photo-anode with complete morphological and optical characteristics. Additionally, this work highlights the integration of atomistic modeling using DFT to validate the experimental data and explore the dispersion and extinction behavior of the proposed thin film.

2 Experimental work and characterization

H\(_2\)TiO\(_3\) powder was prepared using the sol–gel method from Titanium (iv) Isopropoxide, which was obtained from Advent, dispersed in isopropanol as obtained from Piochem using Triton-X from Sigma Aldrich as a template. Distilled water was added dropwise to the homogenous mixture after stirring for four hours. The mixture was left for two days to form a powder. Then it was filtered and dried. Alternatively, Lithium Titanate was prepared by an hour of continuous grinding of stoichiometric ratios of the prepared H\(_2\)TiO\(_3\) and the Lithium carbonate nanopowder, bought from Merck a 99.9%, in an equal mass of deionized water. Finally, the mixture was calcinated for five hours in a muffle furnace 500 °C.

Following our previous work in [14], the photo-anode layer was prepared [14]. The first 2.5 g of the semiconductor was grinded in 3 ml of Triton-X until a homogenous paste formed. Then 0.75 ml, again of Triton-X, was added to the mixture and grinded. The mixture is then spread equally, using an automatically controlled screen-printing setup to cover a specified portion of the conductive glass electrode on the conductive face, then placed onto a hot plate to allow for the annealing and formation of the mesoporous layer of the oxide semiconductor. Upon annealing, the semiconductor turned into a dark colorized brown layer, which was expected to absorb the incident photons better than the white layer, usually obtained using the mesoporous layer of TiO\(_2\) due to the better color absorption of the dark color of the layer. The morphological properties of the prepared samples were analyzed using SEM (Quattro s-Thermo Scientific), EDX (Quattro s-Thermo Scientific), Mapping (Quattro s-Thermo Scientific), XRD (Empyrean Malver Panalytical), AFM (alpha300
Atomic Force Microscope from WITec GmbH), and UV–Vis–NIR (Cary 500).

3 DFT atomistic modeling

The wave function (WF) is the solution of the Schrödinger equation that describes the particle-wave characteristics mathematically in the quantum mechanics paradigm [25]. Since the WF is described mathematically by a complex-valued probability amplitude function, its value for a given particle is related to the likelihood of the particle being there at the time of measurement [26, 27]. The complexity of solving the WF for many electron systems has initiated several approximations to solve such problems [28, 29]. According to the Hartree–Fock (HF) approximation [30], the WF depends on four variables: the three electron coordinates and its spin, assuming the nucleus position to be fixed. In the early ’60s of the last century, Kohn–Sham and Hohenberg introduced a new concept for energy determination of quantum systems [31]. The concept utilizes the electron density, which is a physical observable and depends only on three coordinates, to determine the whole system’s molecule energy and other physical properties. Since their work depends on the system electron density, the theory was called the Density Functional Theory (DFT) [28, 29].

Various numerical solvers have been introduced in the literature to perform DFT calculations. VASP “Vienna Ab initio Simulation Package” is considered one of these numerical solvers [32]. VASP performs ab-initio quantum mechanical calculations using one of two methods: the pseudo-potentials method or the projector-augmented wave method (PAW) with a plane wave basis set [32]. Additionally, VASP supports the calculation of post-DFT corrections such as hybrid functional, which mixes the DFT and HF exchange [33]. The VASP is seeded by four input files INCAR, POTCAR, POSCAR, and K-POINTS [32]. The INCAR is the central input file of VASP, while the POTCAR contains the pseudo-potential for each atomic species used in the calculation [32]. The POSCAR contains the lattice geometry and the ionic positions. Finally, the K-POINTS contains the k-point
coordinates and weights or the mesh size for creating the k-point grid [32, 33]. In the current study, LTO has been simulated using VASP. Simulations were conducted on our computational unit of 2 × Xeon Gold 6240 2.6G processor, with a total of 36 cores and 24 MB Cache, each 32 GB RAM, supported by 2 × 480 GB SSD HD. The simulation results were demonstrated as HOMO–LUMO gap to estimate the material energy’s band gap. In addition, the DFT post-calculation was used to describe the imaginary part of the material permittivity ($\varepsilon''$).

Finally, a Finite Difference Time Domain (FDTD) Maxwell’s equation solver, MEEP, is used to simulate the UV–Vis–NIR spectra for the proposed thin film [34]. The material dispersion and extinction parameters are seeded to the FDTD model in Lorentz–Dude (LD) coefficients [10]. Herein, we use our previously introduced LD model for semiconductors [35].

4 Experimental results

4.1 LTO nanoparticles characterizations

Following the recipe presented in Sect. 2, the LTO powder was prepared and characterized. SEM measurements, see Fig. 1a–c, showed a mostly uniform distribution of particles in shape and size. The prepared powder showed accumulations of particles structures in numerous areas. An agglomerated particle is shown clearly in Fig. 1a to have a rod-like shape of a length around 100 μm. As shown in Fig. 1b, the particles on the surface of the agglomerated molecules are tiny in size of an approximate diameter of 100 nm. It also shows a smaller agglomeration of particles onto the surface of the larger particle. The particles size was verified under the electron microscope, shown below in Fig. 1c. The image of lithium titanate is obtained at a magnification of ×60,000 shows a particle size of approximately 0.10 μm.

According to Hovington et al. [36], detecting lithium and other light chemicals on an energy-dispersive X-ray analysis is considered a challenge [36]. The generated rays are of very low intensity to detect the targeted components; thus, detecting such small components requires high precision. Herein, the energy-dispersive X-ray detects a low percentage of lithium atoms due to the low-energy waves transmitted. Instead, oxygen showed a dominating percentage with minor Titania atoms observed. However, the measurement is still needed for band-gap detection. X-ray diffraction pattern for the nanopowder samples was also conducted in Fig. 2. Using the reference code 01-074-2257 and 00-033-0831 for the Lithium titanate phase, the peak list obtained was compared to the reference, showing that two phases were obtained in which the peak list can be matched. The more dominant phase has a monoclinic structure, while the other is a cubic crystal. Even
though the sharp peaks can be distinctively recognized, some distortion can also be seen. This indicates that the sample has limited crystallinity.

### 4.2 LTO thin-film characterizations

Thin-film characterization was carried out after spreading the LTO powder on conducting electrodes supported on glass. The measurement obtained from the scanning electron microscope at a magnification of $\times 300$ is shown in Fig. 1d. It verifies the formation of the compact layer of the prepared powder after annealing. The image shows rod structures, also of an average size of 100 $\mu$m, accompanied with some bulky foreign bodies, which may refer to the structure of the solvents used to prepare the thin film. In addition, the thin-film content was addressed using mapping, as shown in Fig. 3. Herein, the experimentally measured band gap tends to be around 3.5 eV. Finally, the thin-film roughness was measured using an atomic force microscope (AFM), as demonstrated in Fig. 4. The measurements showed a very acceptable roughness of around 2.50 nm in a $(0.5 \mu m)^2$ region.
5 DFT model results and discussion

Using the DFT VASP model introduced in Sect. 3, LTO is selected as the layer under test. For the sake of minimum processing, a cubic structure was studied to demonstrate the optoelectronic properties of LTO. Initially, the structure is relaxed for estimating the lattice constant. Consequently, the relaxed structure is modeled to sketch the energy band diagram (see Fig. 5) along with the density of states (DOS). Knowing that the generalized gradient approximation (GGA) underestimates the band gaps in DFT simulations [37], the hybrid nonlocal exchange–correlation functional (HSE) is used to determine the LTO band gap. Referring to Fig. 5, LTO seems an indirect band-gap semiconductor with a 3.55 eV band gap. The estimated band gap agrees with the experimentally measured energy-dispersive X-ray analysis data and the previously reported data from the literature [38].

In addition to the DOS presented in Fig. 5, the imaginary part of the LTO permittivity as a semiconductor was extracted from the DFT model, as demonstrated in Fig. 6. The imaginary part of the
permittivity, $\text{Im}(\varepsilon)$, has a significant impact on the optical model as it represents the extinction optical response of the material in terms of absorption and scattering. It can be observed that the $\text{Im}(\varepsilon)$ spectrum is with a peak at 275 nm, which is basically due to the high band gap of 3.55 eV. Accordingly, LTO has shown such a UV-absorbing spectrum.

The FDTD simulation platform, MEEP, is utilized as Maxwell’s equation solver for optical modeling. The model is simulated as a thin film of 5 $\mu$m thickness with two Gaussian beams centered at 550 nm to emulate the TE and TM optical waves. The material dispersion and extinction were inputted using LD-fitting coefficients. Simulations are made using the LD-fitting parameters: $\varepsilon_\infty = 1.12$, $\sigma_1 = 1.5485 \ v + 41$, $\omega_1 = 0.34335$, $\Gamma_1 = 0.018745$, $\sigma_2 = 9.14589$, $\omega_2 = 0.42358$, $\Gamma_2 = 2.12145$, $\sigma_3 = 0.75448$, $\omega_3 = 2.788945$, $\Gamma_3 = 2.72123$, $\sigma_4 = 0.08745$, $\omega_4 = 1.24558$, $\Gamma_4 = 0.87754$, $\sigma_5 = 0.034589$, $\omega_5 = 0.57921$, and $\Gamma_5 = 0.03564$.

![Fig. 6](image.png)

**Fig. 6** The imaginary part of the permittivity (primary vertical axis to the left), extracted from the DFT model and the UV–Vis–NIR numerically simulated spectrum (secondary vertical axis to the right) using MEEP for LTO, with experimentally measured spectrum for validation. The dispersion and extinction were inputted using LD-fitting coefficients. Simulations are made using the LD-fitting parameters: $\varepsilon_\infty = 1.12$, $\sigma_1 = 1.5485 \ v + 41$, $\omega_1 = 0.34335$, $\Gamma_1 = 0.018745$, $\sigma_2 = 9.14589$, $\omega_2 = 0.42358$, $\Gamma_2 = 2.12145$, $\sigma_3 = 0.75448$, $\omega_3 = 2.788945$, $\Gamma_3 = 2.72123$, $\sigma_4 = 0.08745$, $\omega_4 = 1.24558$, $\Gamma_4 = 0.87754$, $\sigma_5 = 0.034589$, $\omega_5 = 0.57921$, and $\Gamma_5 = 0.03564$.

with the material refractive index, applying the same procedure as in [10]. A thin film of 4.28 $\mu$m thickness was observed. The comparison between the simulation data and the experimental measurements in Fig. 6 indicates a very acceptable argument with an average root-mean-square error of 3.78%.

It can be highlighted that the prepared LTO layer can be integrated into various solar cells architectures for photon management applications. Specifically, LTO can be used as an anode electrode in DSSC applications, where the dye functionalizes visible photons absorption. Moreover, the LTO can play an exciting role in perovskite over silicon application, where LTO can perfectly match the visible silicon spectrum, getting rid of hot UV photons, which increases cell temperature. Therefore, we consider LTO a potential layer in various solar cell applications.

6 Conclusion

This work presents an attempt to prepare LTO as a high band-gap semiconductor material capable of being integrated into solar cells applications. The energy band gap of 3.55 eV was calculated experimentally and validated numerically with the aid of the DFT model. The density of states and extinction spectrum were captured from the DFT model seeded to the MEEP optical simulator. Finally, the $T$--$\lambda$ transmission spectrum is simulated using the FDTD Maxwell equation solving platform, with experimental reaching mean-square error of 3.78%, for 4.28 $\mu$m thin-film thickness.

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Authors’ contributions

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Data availability

The data that support the findings of this study are available as follows: https://www.mathworks.com/matlabcentral/fileexchange/76474-dssc-optical-modelling. Any other data supporting this study’s findings are available from the corresponding author upon reasonable request.

Code availability

Not applicable’ for that section.

Declarations

Conflict of interest  The authors declare no conflict of interest.

Ethics approval  Not applicable for that section.

Informed consent  All authors confirm their participation in this paper.

Consent for publication  All authors accept the publication rules applied by the journal.

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References

1. J. Yang, Y. Wang, B. Xue et al., Sci. Total Environ. 795, 148791 (2021)
2. S. Ahmed, Z. Li, M.S. Javed, T. Ma, Mater. Today Energy 21, 100776 (2021)
3. L. Sucupira, J. Castro-Gomes, CivEng 2, 852 (2021)
4. M. Tawalbeh, A. Al-Othman, F. Kafiah, E. Abdelsalam, F. Almomani, M. Alkasrawi, Sci. Total Environ. 759, 143528 (2021)
5. C. Liu, C. Xiao, C. Xie, W. Li, Nano Energy 89, 106399 (2021)
6. M Kokkonen, P Talebi, J Zhou, et al. (2021) J. Mater. Chem. A.
7. R. Liu, L. Wang, Y. Fan, Z. Li, S. Pang, RSC Adv. 10, 11551 (2020)
8. S.O. Abdellatif, S. Josten, A.S.G. Khalil, D. Erni, F. Marlow, IEEE J. Photovolt. (2020). https://doi.org/10.1109/JPHOTOV.2020.2965399
9. S.O. Abdellatif, S. Josten, A.S. Khalil, D. Erni, F. Marlow, IEEE J. Photovolt. 10, 522 (2020)
10. S. Abdellatif, P. Sharifi, K. Kirah et al., Microporous Mesoporous Mater. 264, 84 (2018)
11. A.A. Eid, Z.S. Ismail, S.O. Abdellatif, 2020 2nd Novel Intelligent and Leading Emerging Sciences Conference (NILES) (2020)
12. T. Hatem, Z. Ismail, M.G. Elmahgary, R. Ghannam, M.A. Ahmed, S.O. Abdellatif, IEEE Trans Electron Dev (2021). https://doi.org/10.1109/TED.2021.3101780
13. M Hassan, N Iskander, S Abdellatif, K Kirah, H Ghali (2020) Investigating parasitic resistance of mesoporous-based solar cells with respect to thin-film and conventional solar cells. SPIE,
14. T. Hatem, M.G. Elmahgary, R. Ghannam, M.A. Ahmed, S.O. Abdellatif, J. Mater. Sci.: Mater. Electron. 32, 25318 (2021). https://doi.org/10.1007/s10854-021-06990-4
15. R. Singh, N Kaur, A. Mahajan, Sol. Energy 226, 31 (2021)
16. H.P. Wante, J. Aidan, S.C. Ezike, Curr. Res. Green Sustain. Chem. 4, 100218 (2021)
17. G.-H. Kim, D.S. Kim, Joule 5, 1033 (2021)
18. J. Chen, N.G. Park, Adv. Mater. 31, 1803019 (2019)
19. T. Lindgren, H. Wang, N. Beermann, L. Vayssieres, A. Hagfeldt, S.-E. Lindquist, Sol. Energy Mater. Sol. Cells 71, 231 (2002)
20. K. Sayama, A. Nomura, Z. Zou, R. Abe, Y. Abe, H. Arakawa, Chem. Commun. 23, 2908 (2003)
21. J. Zhang, W. Luo, W. Li et al., Electrochem. Commun. 22, 49 (2012)
22. A. Iqbal, N. Ibrahim, N.R.A. Rahman et al., Surfaces 3, 301 (2020)
23. Z. Li, Y. Chen, J. Shen, X. Cui, New J. Chem. 41, 6305 (2017)
24. E.M. Hashem, M.A. Hamza, A.N. El-Shazly, M.F. Sanad, M.M. Hassan, S.O. Abdellatif, Nanotechnology 32, 085701 (2020). https://doi.org/10.1088/1361-6528/abca29
25. X.-Y. Pan, V. Sahni, L. Massa, Phys. Rev. Lett. 93, 130401 (2004)
26. G. Alfimov, P. Kevrekidis, V. Konotop, M. Salerno, Phys. Rev. E 66, 046608 (2002)
27. M. Taut, J. Phys.: Condens. Matter 12, 3689 (2000)
28. M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, J. Catal. 211, 1 (2002)
29. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 132, 154104 (2010)
30. D. Pfannkuche, V. Gudmundsson, P.A. Maksym, Phys. Rev. B 47, 2244 (1993)
31. G.E. Bauer, Phys. Rev. B 27, 5912 (1983)
32. J. Hafner, J. Comput. Chem. 29, 2044 (2008)
33. J. Hafner, Comput. Phys. Commun. 177, 6 (2007)
34. S.O. Abdellatif, K. Kirah, D. Erni, F. Marlow, Appl. Opt. 59, 10432 (2020). https://doi.org/10.1364/AO.408576
35. S. Abdellatif, R. Ghanaam, A. Khalil, Appl. Opt. 53, 3294 (2014)
36. P. Hovington, V. Timoshevskii, S. Burgess et al., Scanning 38, 571 (2016)
37. L. Lang, J.-H. Yang, H.-R. Liu, H. Xiang, X. Gong, Phys. Lett. A 378, 290 (2014)
38. S. Lkhagvajav, N. Tsogbadrakh, E. Enkhbayar, S. Galsan, P. Altantsog, Mongol. J. Chem. 20, 7 (2019)

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