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Boosting Dye-sensitized Solar Cell Efficiency using AgVO_3 -doped TiO_2 Active layer

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Abstract—Dye sensitized solar cells (DSSCs) have shown great potential in low and self-powered nano/micro-scale applications, due to their low fabrication costs, semi-transparency in the visible spectrum, diffused light harvesting capabilities and their lead-free structure. However, DSSC efficiencies are still relatively low due to their limited absorption capabilities in the active mesoporous layer. The current study demonstrates an attempt to boost the overall conversion efficiency of DSSC by narrowing the energy bandgap of the mesoporous TiO_2 active layer. AgVO_3 is utilized in doping the mesoporous layer, seeking for a visible absorption shift from 3.2 eV to 2.6 eV. Additionally, natural organic beetroot dye is used while keeping DSSC with N719 dye as a bare cell. Morphological, optical as well as electrical characterization results were obtained for both thin-film and complete solar cells. The fabricated cell showed an overall harvested power of 19.24 mW, capable of operating various low-power sensing applications.

Index Terms— AgVO_3 doping, Dye Sensitized Solar Cells, Mesoporous TiO_2 , Natural dye.

I. INTRODUCTION

TiO_2 films composed of nanoparticles in the range from 10 to 30 nm can have a roughness factor (the actual surface area to the apparent one) reaching 1000 [1]. Therefore, the amount of dye adsorbed in a DSSC is drastically increased due to the much larger accessible internal surface when the mesoporous TiO_2 is used. In fact, the space-filling capability of the dye can reach almost 100% over a wide range in the visible region [1]. By virtue of comparison, the amount of adsorbed dyes on the surface of single-crystals and poly-crystal materials is quite small, causing only about 1% absorption even at the peak wavelength [2]. Such properties nominate mesoporous TiO_2 to be integrated in various optoelectronic applications [1]–[7]. One of these applications as an active layer in dye sensitized solar cells (DSSC) [7]–[9].

The absorption mechanism in the DSSC is mainly rely on the visible absorption due to the absorbed dye, as TiO_2

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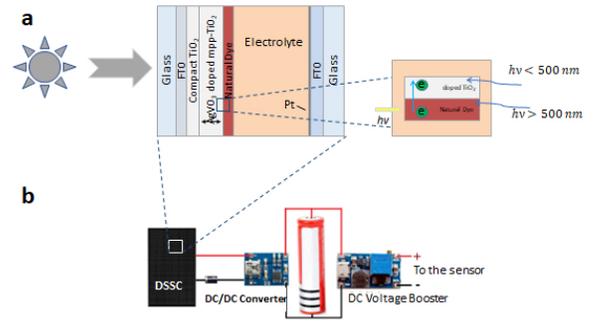


Fig. 1. (a) Architecture of our DSSC (b) Diagram showing the location of the DSSC in our underwater light harvesting unit.

is an UV absorber (3.2 eV) [3], [5]–[9]. Consequently, the reported DSSC efficiency is rarely reaching 10% [4], [10], [11]. Previous attempts in the literature acted to enhance the DSSC efficiency either by adding new trapping structures or by customizing the optical properties of the mesoporous TiO_2 layer. In such context the AgVO_3 -doped TiO_2 thin film can be deposited using a simple sol-gel method [4]. Such doping can narrow-down the energy bandgap, turning mesoporous TiO_2 to be a visible light absorber. Concerning the used dye, previous attempts were demonstrated with commercial N719 dyes [1], [12], [13]. Alternatively, other attempts replaced the inorganic N719 dye with a low-cost organic dye based on beetroot. Organic beetroot dye recorded acceptable sustainability in previous attempts in the literature as well as matched optical spectrum with mesoporous TiO_2 [14], [15].

The work investigated in this paper demonstrates the impact of AgVO_3 doping on a mesoporous TiO_2 layer used in organic-based dye sensitized solar cells. Experimentally segmented and complete solar cells have been fabricated and characterized to evaluate the effect of doping on the overall conversion efficiency. The fabricated cell showed acceptable output characteristics with 19.24 mW harvested power, as well as V_{oc} of 0.5 V and I_{sc} of 21 mA/cm^2 . Herein, our fabricated cell can be used to harvest light for satisfying the energy demands of a micro/nano-sensing unit. The low power sensor was normally operated via the connected DC battery (c.f. 1).

II. EXPERIMENTAL WORK AND CHARACTERIZATION

This section describes the fabrication process for a complete DSSC with organic dye and various AgVO_3 -doping concen-

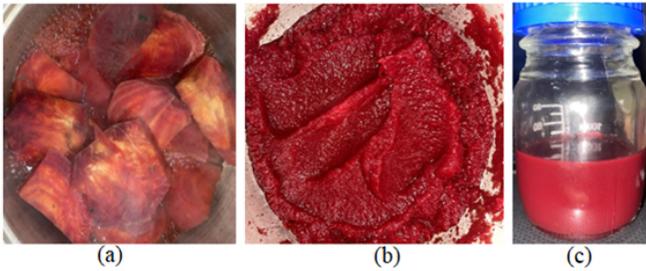


Fig. 2. (a) Beet in boiling water (b) blended beet (c) natural beet extracted dye.

trations, applying a bottom-up approach. Additionally, all morphological, optical, and electrical characterization procedures are explained.

A. Materials

Titanium (IV) Isopropoxide ($C_12H_28O_4Ti$, 97%), Carboxy methyl cellulose sodium salt (CMC) and Isopropyl alcohol (C_3H_8O) were purchased from Sigma Aldrich for preparing TiO_2 powder. Silver nitrate ($AgNO_3$) and Sodium vanadate ($NaVO_3$) were purchased from Merck and used in preparation of the doped material. Acetonitrile (CH_3CN), Sodium Hydroxide ($NaOH$), Ethylene Glycol ($C_2H_6O_2$), Fluorescent dye, Fluorine-doped tin oxide (FTO), Iodine (I) G. R. grade, 99.8 %, Potassium Iodide (KI), were also purchased from Sigma Aldrich. N719 dye as well as natural dye, extracted from “Beet” and has a dark reddish-purple color, were used (see Figure 2).

B. TiO_2 Nanoparticle Preparation and Deposition

TiO_2 nanoparticles were prepared using the sol-gel method. 40 mL of Titanium (IV) Isopropoxide and 400 mL of Isopropyl alcohol (IPA) were mixed on a magnetic stirrer for 30 min at a speed of 100 rpm. Next, distilled water was added (drop by drop using a pipette) until a gel started to form. The solution was left for 2 days before it was later filtered, dried, grinded, then calcinated for 3 hours at $500^\circ C$. For paste preparation, 2.5 g of the prepared nanoparticles were added to 3 mL of CMC. The mixture was then grinded until it achieved the required homogeneity. Finally, 0.75 mL of IPA was added to the mixture and grinded again. The film was screen printed on a glass substrate, as described in our previous work in [1], [12], [13].

C. Ag-doing

Silver Vanadate ($AgVO_3$) was produced from the reacting sodium vanadate ($NaVO_3$) and silver nitrate ($AgNO_3$): “ $NaVO_3 + AgNO_3 \rightarrow NaNO_3 + AgVO_3$ ”. $NaVO_3$ (1.5 gm) and $AgNO_3$ (2.09 gm) were placed with 50 mL of distilled water on the magnetic stirrer until the crystals were completely dissolved in water and the solution was colorless. Next, the sodium vanadate solution was added drop by drop to the silver nitrate solution while stirring for 2 hours, until it turned into a yellowish mustard color. Finally, after placing the mixture

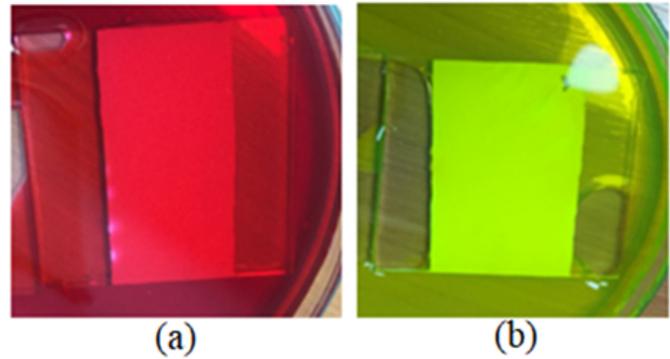


Fig. 3. Thin layer of mp- TiO_2 immersed in (a) beet natural dye (b) N719 dye.

in a probe sonicator for 2 hours, it was filtered, dried, and then grinded. TiO_2 was doped with different concentrations of $AgVO_3$, varying from 0% to 25%. Powders were mixed in a beaker with 50 mL distilled water. Next, the mixture placed in a probe sonicator for 1.5 hours and was again filtered, dried, and then grinded. Doped- TiO_2 pastes were then prepared using the same recipe mention in section 2.2 and were deposited on glass using the screen-printing technique.

D. Segmented and complete DSSCs fabrication

In comparison with our previously published work in [1], [12], [13], [16], we have replaced the commonly used N719 dye with an organic natural dye (detailed recipe is listed table 1). Moreover, mp- TiO_2 was replaced by an $AgVO_3$ -doped mp- TiO_2 layer, as discussed in the previous section. Herein, beetroot was used as a natural organic dye, which has a dark reddish purple color and has good sunlight absorption capabilities [7]. Beetroot-based dye was chosen due to its matched light spectrum, acceptable lifetime as well as significantly reduced cost with respect to commercial N719 dye. For example. one gram of N719 approximately costs 330 euros, while the extracted organic dye costs less than 5% of this [17]. The extraction process was initiated by first rinsing the beetroot with water. They were later peeled and chopped to smaller parts. In a pan, distilled water was boiled with the chopped beetroot for around 15 minutes. After cooling down, the beetroot was squeezed using a hand blender until it turned into a paste. The observed consistency was very thick as shown in Fig 2. A paper filter was then placed in a conical flask with a funnel. By adding pressure, the liquid beet natural dye was extracted, filtered, and ready for use.

Seeking for a bare cell, yellowish green N719 dye was prepared. The prepared concentration of the synthetic dye was 2×10^{-5} Molar. The medium is alkaline by using $NaOH$ to increase the solubility of the dye in distilled water (see fig. 3). All DSSCs were sealed using a hot press at a temperature of $120^\circ C$.

E. Characterization

The crystalline size and structure of the prepared nanoparticles were estimated by P Analytical X’PERT MPD diffractometer using ($Cu [K\alpha_1/K\alpha_2]$) radiation. The diffraction

TABLE I
RECIPE AND PREPARATION OF EACH LAYER FOR DSSCs

Step No.	Step name	Needed Chemicals	Description
1	Ethylene-glycol and Acetonitrile-based electrolyte	- 0.24 g of I ₂ . - 5 mL of Ethylene-glycol. - 20 mL of Acetonitrile. - 2.49 g of KI.	- Add 0.24 g I ₂ along with 2.49 g KI to 5 ml Ethylene-glycol. - Add to the mixture 20 mL of Acetonitrile. - Mix on magnetic stirrer for 30 minutes until the solution is homogeneous.
2	Triton-X based TiO ₂ paste for mesoporous layer.	- 2.5 g of TiO ₂ powder. - 3 mL Triton-X polymer. - 0.75 ml IPA.	- Add 2.5 g of TiO ₂ powder with 3 mL Triton-X polymer. - Pestle until mixture is homogeneous. - Add 0.75 ml of IPA to the mixture and pestle again.
3	Compact TiO ₂ layer	- 170 mL of IPA - 12 mL of titanium IPA - 0.4 mL of 2MHCL	- Add IPA and titanium IPA while stirring. - Drop by drop add 2M of HCL. - Stir using magnetic stirrer for over an hour. - Store in a dark place.
4	Graphite on counter electrode	Graphite	To prepare the counter electrode a thin layer of graphite was traced on the FTO side of the counter electrode.

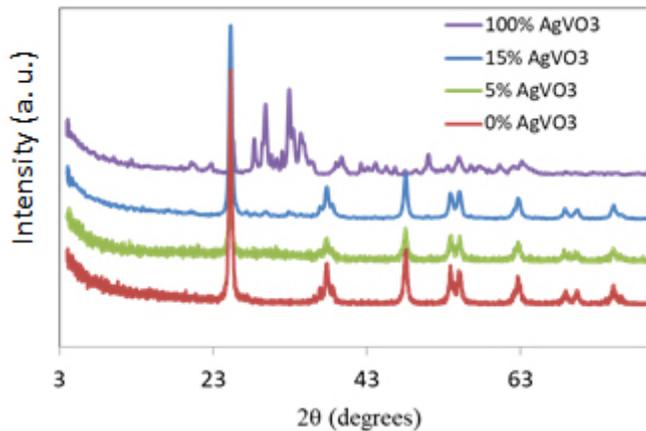


Fig. 4. XRD patterns of TiO₂, TiAg₅ and TiAg₁₅. The diffraction pattern of pure Titania shows several peaks at $2\theta = 25.3^\circ, 36.9^\circ, 37.7^\circ, 38.5^\circ, 48^\circ, 51.9^\circ, 53.8^\circ, 55.1^\circ, 62.6^\circ, 68.7^\circ$ and 75° [JCPDS No. 71-1167 were $a = 3.786 \text{ \AA}$ and $c = 9.507 \text{ \AA}$] referred to Titania anatase phase. These peaks were indexed in order of increasing diffraction angles indicated a body centered tetragonal crystalline structure of Titania crystal.

angle ranges from 10° to 90° with a step of 0.02° with integration time of three s/step were utilized. The morphologies of the samples were analyzed using High resolution transmission electron microscopy (SEM JEOL 6340). To electrically characterize the fabricated DSSCs, an LED-based solar simulator with an integrated NIR-UV-Vis spectrometer and Keithley 2401 current-voltage source meter were used [17]. The optical transmission spectra of the fabricated as well as semifinished DSSCs is measured through a V-770 UV-Visible/NIR Spectrophotometer was used, which has a wavelength range from 190 nm to 2700 nm.

III. RESULTS AND DISCUSSIONS

A. TiO₂ nanoparticles characterizations

Following the AgVO₃-doped TiO₂ nanoparticles recipe introduced in section 2, XRD analysis was carried to investigate the crystal structure of the prepared nanoparticles. XRD was conducted for TiO₂, AgVO₃, TiO₂ doped with 5% to 25% to ensure that the required structures were formed. Fig. 4 shows the XRD patterns of TiO₂, TiAg₅ and TiAg₁₅. The XRD pattern of the nanocomposite shows the existence of broad peak revealing the reduction in Titania crystallites upon incorporation of bismuth vanadate. The diffraction pattern of pure Titania shows several peaks at $2\theta = 25.3^\circ, 36.9^\circ, 37.7^\circ, 38.5^\circ, 48^\circ, 51.9^\circ, 53.8^\circ, 55.1^\circ, 62.6^\circ, 68.7^\circ$ and 75° [JCPDS No. 71-1167 were $a = 3.786 \text{ \AA}$ and $c = 9.507 \text{ \AA}$] referred to Titania anatase phase. These peaks were indexed in order of increasing diffraction angles indicated a body centered tetragonal crystalline structure of Titania crystal. The XRD pattern of the nanocomposite shows the existence of broad peak revealing the reduction in Titania crystallites upon incorporation of bismuth vanadate. This result reflects the strong chemical interaction between AgVO₃ and anatase TiO₂ to form titanium vanadium hydroxide.

subsection TiO₂ thin film characterizations Using the recipe discussed in section 2, TiO₂ paste was deposited on microscopic glass substrates. Three sets of samples were prepared using TiO₂ paste as well as AgVO₃-doped. SEM characterization analysis is carried out for the deposited thin layer to determine the surface characteristics, size and shape of particles, composition, and arrangement of atoms in the sample. Measurements were conducted for TiO₂, TiO₂ doped with 5% to 25%. As shown in Fig. 5, the anatase titanium dioxide mesoporous layer which is prepared by sol-gel method [1, 13] has a homogenous structure and is highly crystalline with spherical agglomerated particles.

EDX characterization analysis and SEM-mapping are attached in Fig. 6 and 7. EDX characterization analysis is carried out to determine and identify the elements present in the sample with information about their percentages (see Fig. 6).

Analyses illustrates the elements presented in TiO₂ are Ti and O. while the elements presented in TiO₂ doped 5% and 15% are Ti, O, Ag, and V, with the indicated percentages in the graphs (c.f. Fig. 6-b and c). Finally, as shown in Fig. 7, the concentration of elements in the TiO₂ doped with 5% AgVO₃ was investigated. This validates the success of the doping process.

B. Optical characterizations

We compared the absorption spectrum of beetroot dye standard N719 dye (see figure 8). It can be observed that the natural beetroot dye, with peak absorption around 550 nm (centralized visible absorption spectrum), is more appropriate for the proposed DSSC compared with N719 dye. This is due to the enhanced absorption of the doped TiO₂ layer, making it capable of absorbing near ultra-violet photons in the visible portion of the spectrum (350 nm to 500 nm). Accordingly, the integration of the AgVO₃ dop ed TiO₂ layer with the

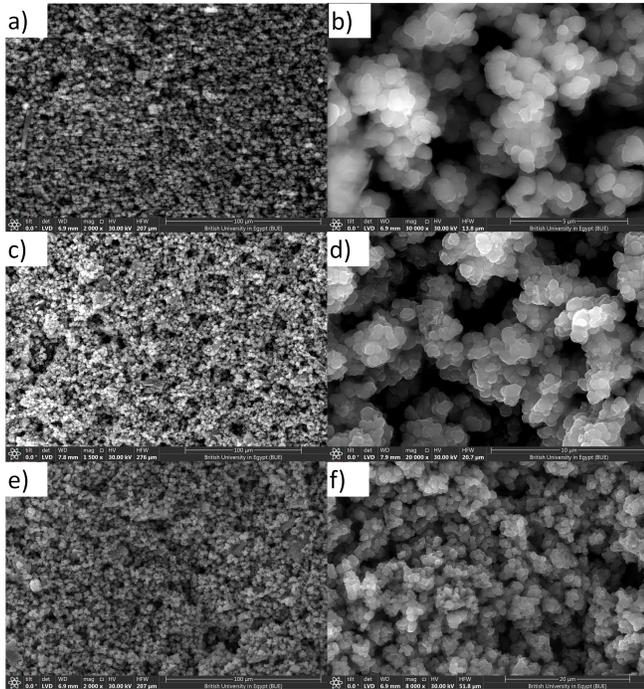


Fig. 5. SEM for (a) and (b) TiO_2 , (c) and (d) TiO_2 doped with 5% AgVO_3 and (e) and (f) TiO_2 doped with 15% AgVO_3 .

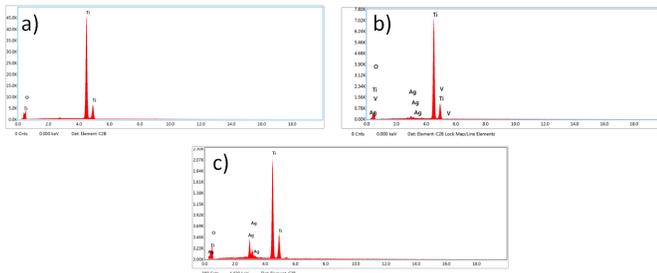


Fig. 6. EDX for (a) TiO_2 (b) TiO_2 doped with 5% AgVO_3 and (c) TiO_2 doped with 15% AgVO_3 .

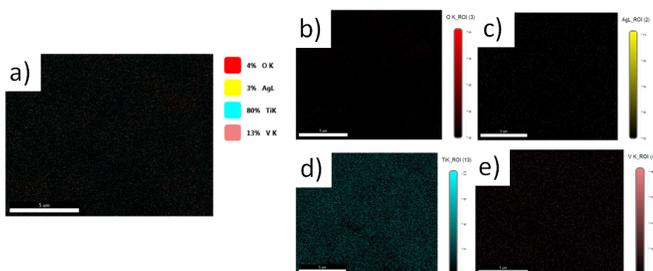


Fig. 7. Mapping analysis for titanium dioxide doped with 5% concentration of silver vanadate, (b) to (e) Color intensity and concentration for each element in the 5% doped sample.

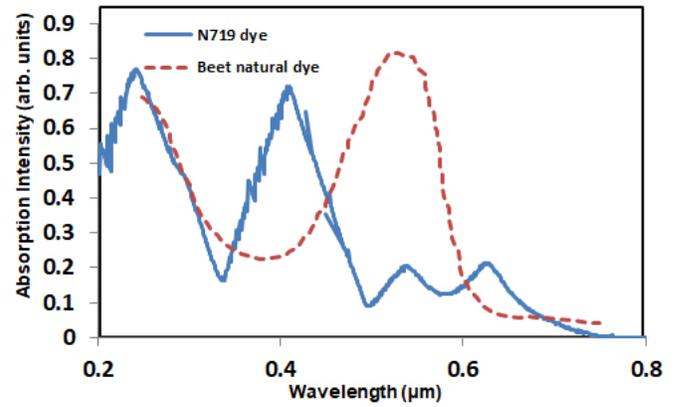


Fig. 8. Absorption spectra for (a) N719 and (b) Beetroot dye.

beetroot natural dye will broaden the absorption spectrum of the effective active layer in DSSC.

C. Electrical characterizations

The J-V characteristic curves for the fabricated DSSCs are shown in Fig. 9. In the current study we investigated the impact of both AgVO_3 doping as well as the beetroot dye. Firstly, it can be observed that the higher the doping the rate the higher the short-circuit current density. Maximum is obtained when the doping rate reached 15% with current density of 21 mA/cm^2 . This condition represents the maximum efficiency of around 6.1 % with total extracted power around 19.24 mW. Consequently, by referring to the bare cell with N719 dye, still the beetroot dye recorded higher current as well as efficiency with respect to N719 DSSC. Beetroot dye showed an enhanced performance by nearly 10% while considering N719 dye as a reference keeping the doping level constant in both as 15% (cf. Fig. 9). This agrees with the interpretation proposed earlier related to the matching in the spectra between organic beetroot dye and the mesoporous TiO_2 layer with narrowed energy bandgap. Herein, a merged absorption profile with visible absorption overlapping is resulted that can maximize the absorption in the active layer. Accordingly, we can describe the proposed DSSC as a double absorption effect DSSC, where both the AgVO_3 doped TiO_2 and the dye are contributing to the absorption mechanism. By referring to the literature, we can figure out that the measured efficiency with 15% doping and beetroot dye enhanced the efficiency of the proposed DSSC from 2.1 % (see reported efficiency in [9], under DSSC-A samples) to nearly 6.1%. Other literature attempts recorded higher efficiencies [16], however the cost parameter is very considerable here as a trade-off against efficiency. Our proposed cell can be categorized as a very low cost, simple and low-temperature fabricated cell.

IV. CONCLUSION

This work presents a boosted 6.1% DSSC through narrowing the energy bandgap of the active mesoporous TiO_2 layer as well as integrating a natural dye. Mesoporous TiO_2 is treated with 15% of AgVO_3 to reach an energy bandgap of

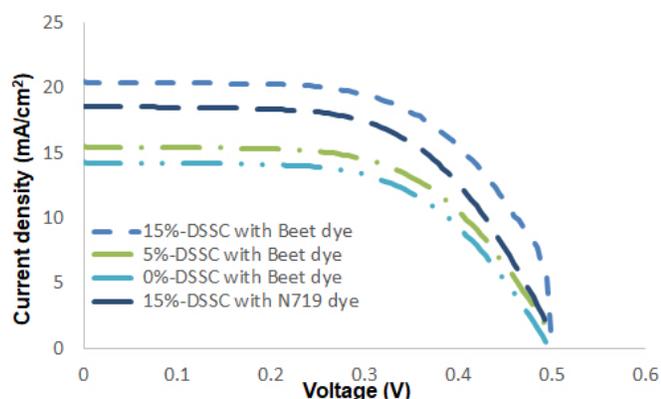


Fig. 9. J-V characteristic curves for fabricated DSSCs with N719 dye and Beetroot dye associated with variable doping level of AgVO_3 in the mesoporous active layer.

2.6eV. The optimized cell with energy harvesting density of 19.24 mW was recorded. The proposed cell showed enhanced performance with respect to a bare cell fabricated with N719 dye as well as similar recipes reported data in the literature. The harvested output power is capable of operating various IoT low power applications towards a self-power sensor.

REFERENCES

- [1] S. Abdellatif, P. Sharifi, K. Kirah, R. Ghannam, A. Khalil, D. Erni, and F. Marlow, "Refractive index and scattering of porous TiO_2 films," *Microporous and Mesoporous Materials*, vol. 264, pp. 84–91, 2018.
- [2] B. O'regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films," *nature*, vol. 353, no. 6346, pp. 737–740, 1991.
- [3] C.-W. Luo, A. P. Thilakan, J.-X. Li, T.-P. Chen, S.-S. Li, C.-W. Chen, A. Yabushita, M. Osada, K. Tsukagoshi, and T. Sasaki, "Uv degradation mechanism of TiO_2 -based perovskite solar cells studied by pump-probe spectroscopy," in *Photonics for Solar Energy Systems VIII*, vol. 11366. International Society for Optics and Photonics, 2020, p. 113660V. [Online]. Available: <https://doi.org/10.1117/12.2554174>
- [4] D. Dey, N. Halder, K. P. Misra, S. Chattopadhyay, S. K. Jain, P. Bera, N. Kumar, and A. K. Mukhopadhyay, "Systematic study on the effect of ag doping in shaping the magnetic properties of sol-gel derived TiO_2 nanoparticles," *Ceramics International*, vol. 46, no. 17, pp. 27 832–27 848, 2020.
- [5] T. A. Egerton, N. J. Everall, J. A. Mattinson, L. M. Kessell, and I. R. Tooley, "Interaction of TiO_2 nano-particles with organic uv absorbers," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 193, no. 1, pp. 10–17, 2008.
- [6] Y. Zhang, G. Li, Y. Wu, Y. Luo, and L. Zhang, "The formation of mesoporous TiO_2 spheres via a facile chemical process," *The Journal of Physical Chemistry B*, vol. 109, no. 12, pp. 5478–5481, 2005.
- [7] S. Sathyajothi, R. Jayavel, and A. C. Dhanemozhi, "The fabrication of natural dye sensitized solar cell (dssc) based on TiO_2 using henna and beetroot dye extracts," *Materials Today: Proceedings*, vol. 4, no. 2, pp. 668–676, 2017.
- [8] K. H. Ko, Y. C. Lee, and Y. J. Jung, "Enhanced efficiency of dye-sensitized TiO_2 solar cells (dssc) by doping of metal ions," *Journal of colloid and interface science*, vol. 283, no. 2, pp. 482–487, 2005.
- [9] G. Deogratias, N. Seriani, T. Pogrebnaya, and A. Pogrebnoi, "Tuning optoelectronic properties of triphenylamine based dyes through variation of pi-conjugated units and anchoring groups: A dft/td-dft investigation," *Journal of Molecular Graphics and Modelling*, vol. 94, p. 107480, 2020.
- [10] M. A. Liaqat, Z. Hussain, Z. Khan, M. A. Akram, and A. Shuja, "Effects of ag doping on compact TiO_2 thin films synthesized via one-step sol-gel route and deposited by spin coating technique," *Journal of Materials Science: Materials in Electronics*, vol. 31, no. 9, pp. 7172–7181, 2020.
- [11] E. M. Hashem, M. A. Hamza, A. N. El-Shazly, M. F. Sanad, M. M. Hassan, and S. O. Abdellatif, "Investigating the uv absorption capabilities in novel Ag/ZnO ternary nanocomposite for optoelectronic devices," *Nanotechnology*, vol. 32, no. 8, p. 085701, 2020. [Online]. Available: <http://dx.doi.org/10.1088/1361-6528/abca29>
- [12] S. Abdellatif, S. Josten, P. Sharifi, K. Kirah, R. Ghannam, A. Khalil, D. Erni, and F. Marlow, "Optical investigation of porous TiO_2 in mesostructured solar cells," in *Physics and Simulation of Optoelectronic Devices XXVI*, vol. 10526. International Society for Optics and Photonics, 2018, p. 105260A.
- [13] S. O. Abdellatif, S. Josten, A. S. Khalil, D. Erni, and F. Marlow, "Transparency and diffused light efficiency of dye-sensitized solar cells: Tuning and a new figure of merit," *IEEE Journal of Photovoltaics*, vol. 10, no. 2, pp. 522–530, 2020.
- [14] R. Grisorio, L. De Marco, C. Baldisserrri, F. Martina, M. Serantoni, G. Gigli, and G. P. Suranna, "Sustainability of organic dye-sensitized solar cells: the role of chemical synthesis," *ACS Sustainable Chemistry & Engineering*, vol. 3, no. 4, pp. 770–777, 2015.
- [15] S. Shalini, R. Balasundaraprabhu, T. S. Kumar, N. Prabavathy, S. Senthilarasu, and S. Prasanna, "Status and outlook of sensitizers/dyes used in dye sensitized solar cells (dssc): a review," *International Journal of Energy Research*, vol. 40, no. 10, pp. 1303–1320, 2016.
- [16] M. O. Ahmed, A. K. Madkor, P. Makeen, S. E. I. Betelmal, M. M. Hassan, M. M. Abdelsamee, A. Ayman, M. H. El-Adly, A. Nessim, and S. O. Abdullatif, "Optimizing the artificial lighting in a smart and green glass building-integrated semi-transparent photovoltaics: A multifaceted case study in egypt," *WSEAS Transactions on Environment and Development*, vol. 17, pp. 118–127, 2021.
- [17] M. M. Hassan, A. Sahbel, S. O. Abdellatif, K. A. Kirah, and H. A. Ghali, "Toward low-cost, stable, and uniform high-power led array for solar cells characterization," in *New Concepts in Solar and Thermal Radiation Conversion III*, vol. 11496. International Society for Optics and Photonics, 2020, p. 114960Q.