OPTIMIZATION OF DOPING PROCESS TOWARDS RUTILE-PHASED TITANIUM DIOXIDE NANORODS ARRAY FOR ULTRAVIOLET PHOTODETECTOR APPLICATIONS

SALINA BINTI MOHAMMAD MOKHTAR

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Universiti Tun Hussein Onn Malaysia

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DEDICATION

This thesis was dedicated to my parents; Mohammad Mokhtar bin Mohammad,
Rabiah binti Ibrahim,
and my husband; Mohamad Najib bin Kammalluden

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ABSTRACT

Titanium dioxide has gained attention in current fundamental research for photodetector application. Commercial UV photodetectors uses Si-based materials that have a low bandgap and needed a filter to filter-out visible light wavelengths. For that reason, TiO_2 is widely studied as it has a wide bandgap that absorbs only UV wavelength. Even so, the slow carrier transport of TiO_2 has been considered a drawback that can limit its full potential in these applications. Focusing on the electronic properties of the material, this study used several dopant concentrations to enhance rutile TiO_2 electron concentration and mobility by using niobium (Nb) and boron (B) as dopants in nanorods TiO_2. Well-aligned TiO_2 nanorods were fabricated with 1.00 mL of TiO_2 precursor as a preliminary study. Herein, the Nb and B-doped rutile TiO_2 nanorods were fabricated by using hydrothermal method with FTO as a substrate. Based on the finding, doping process was successfully done with confirmation on the presence of Nb and B dopants in TiO_2 lattice by XPS spectroscopy. Photocurrent analysis of the TiO_2 nanorods shows increasing current approximately 2.3 times larger than undoped TiO_2 for 0.25 w.t.% Nb doped, and 1.8 times larger for 1.00 w.t.% of B doped with bandgap of 3.09 and 3.04 eV, respectively. While B doping does not give significant changes to the nanorod, Nb dopant inhibits nucleation sites on the FTO thus reducing the density of nanorods in high doping concentration. Annealing treatment was done to enhance the crystallinity of the nanorods with the annealing temperature varied from 200 to 500 °C. Annealing treatment on both samples showed an increase in the photocurrent with enhancement on the crystallinity of samples at 300 °C annealing temperature. The results prove that electron concentration and mobility of rutile TiO_2 nanorods can be enhanced by using Nb and B dopants. Highly crystalline nanorods can be achieved with annealing treatment at 300 °C that will further enhance the electronic properties of rutile TiO_2 nanorods thus making it beneficial in UV photodetector application.

ABSTRAK

Titanium dioksida telah mendapat perhatian dalam penyelidikan asas untuk aplikasi pengesan foto. Pengesan foto UV komersial menggunakan bahan berasaskan Si yang mempunyai jurang jalur yang rendah dan memerlukan penapis untuk menapis jarak gelombang cahaya yang boleh dilihat. Atas sebab itu, TiO_2 dikaji secara meluas kerana ia mempunyai jurang jalur lebar yang hanya menyerap jarak gelombang UV. Walaupun begitu, pengangkutan pembawa TiO_2 yang perlahan telah dianggap sebagai kelemahan yang boleh mengehadkan potensi penuhnya dalam aplikasi ini. Memfokuskan kepada sifat elektronik bahan, kajian ini menggunakan beberapa kepekatan dopan untuk meningkatkan kepekatan dan mobiliti elektron TiO_2 rutil dengan menggunakan niobium (Nb) dan boron (B) sebagai dopan dalam nanorod TiO_2. Nanorod TiO_2 yang jajar telah dibuat dengan 1.00 mL prekursor TiO_2. Di sini, nanorod TiO_2 rutil terdop Nb dan B telah dibuat dengan menggunakan kaedah hidroterma dengan FTO sebagai substrat. Berdasarkan penemuan, proses doping telah berjaya dilakukan dengan pengesahan kehadiran Nb dan B dopan dalam kekisi TiO_2 oleh spektroskopi XPS. Analisis arus foto bagi nanorod TiO_2 menunjukkan peningkatan arus kira-kira 2.3 kali lebih besar daripada TiO_2 yang tidak didop dengan nilai 0.25 w.t.% oleh dopan Nb, dan 1.8 kali lebih besar dengan nilai 1.00 w.t.% oleh dopan B. Walaupun doping B tidak memberikan perubahan ketara kepada morfologi nanorod, dopan Nb telah menghalang tapak nukleasi diatas FTO sekali gus mengurangkan ketumpatan nanorod dalam kepekatan doping yang tinggi. Rawatan penyepuhlindapan telah dilakukan untuk meningkatkan kehabluran nanorod dengan suhu penyepuhlindapan yang berbeza-beza dari 200 hingga 500 °C. Rawatan penyepuhlindapan pada kedua-dua sampel menunjukkan peningkatan dalam arus foto dan pada kehabluran sampel dengan suhu penyepuhlindapan 300 °C. Ini menunjukkan bahawa kepekatan elektron dan mobiliti nanorod TiO_2 rutil boleh dipertingkatkan dengan menggunakan dopan Nb dan B.

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LIST OF SYMBOLS AND ABBREVIATIONS

°C	-	Degree Celsius
B	-	Boron
C	-	Carbon
CBD	-	Chemical bath deposition
CBM	-	Conduction band minimum
CVD	-	Chemical vapour deposition
D	-	Crystallite size
DI water	-	Deionized water
Eg	-	Bandgap
EIS	-	Electrochemical impedance spectroscopy
EtOH	-	Ethanol
FESEM	-	Field emission scanning electron microscopy
FTO	-	Fluorine-doped tin oxide
FWHM	-	Full-width half-maximum
GaN	-	Gallium nitrite
H2O	-	Water
HCl	-	Hydrochloric acid
ITO	-	Indium-doped tin oxide
Jsc	-	Photocurrent
KCl	-	Potassium chloride
LiCl	-	Lithium chloride
Mg	-	Magnesium
µm	-	Micrometre
N	-	Nitrogen
NaCl	-	Sodium chloride
Nb	-	Niobium
nm	-	Nanometre

NPs	-	Nanoparticles
O	-	Oxygen
OH	-	Hydroxide
PEC	-	Photoelectrochemical
QDs	-	Quantum dots
SiC	-	Silicon carbide
Sn	-	Tin
TBOT	-	Titanium butoxide
TCO	-	Transparent conductive oxide
TEM	-	Transmission electron microscopy
TiO_2	-	Titanium dioxide
Ti	-	Titanium
TiCl4	-	Titanium chloride
TTIP	-	Titanium isopropoxide
UV	-	Ultraviolet
w.t.%	-	Weight percentage
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-ray diffraction
ZnO	-	Zinc oxide

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Titanium dioxide (TiO_2) has emerged as a potential material in UV photoconductive sensor applications. Titanium dioxide has a direct and wide bandgap energy that allows it to strongly absorb UV light. When TiO_2 is illuminated with UV light, electrons from the valence band are excited into the conduction band to give rise to conductivity. The increase in conductivity due to the excitation of electrons under UV irradiation produces a signal that can be used for UV light detection. Photo-detection in the ultraviolet (UV) area has attracted attention due to its numerous applications in industries, instruments, and our daily life. Ultraviolet light is defined as a portion of the electromagnetic spectrum that also includes visible light, radio waves, X-rays and microwave, with wavelength ranging from 100 to 400 nm that can be further subdivided to: Vacuum UV (100-200 nm), UVC (200-280 nm), UVB (280-315 nm), and UVA (316-400 nm) [1]. It has wavelength that is shorter than visible light, but longer than X-rays as shown in Figure 1.1. With the focus being in the UVA, the direct bandgap of TiO_2 at 3.40 - 3.00 eV at room temperature [2], [3] is suitable as UVA energy lies in the range of 3.9 to 3.1 eV.

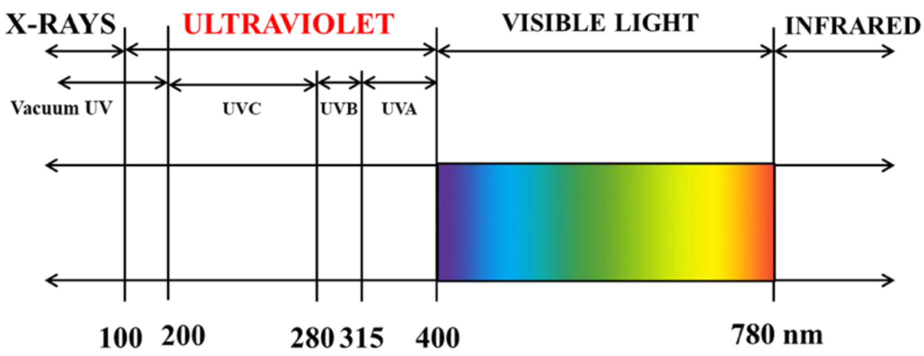

Figure 2.1: Electromagnetic spectrum showing the wavelength of three types of ultraviolet that is UVA, UVB, and UVC

TiO_2 has a melting point of 1825° which implies strong bonds and shows that it is a thermally and chemically resistant material [4]. Rutile, anatase, and brookite are three phases of TiO_2 that are widely known to have existed in either bulk structure or nanoparticles. Rutile has six atoms in a unit cell with each titanium atom is bonded to six oxygen atoms, meanwhile, each oxygen atom bonded to three titanium atoms. With a slightly more distorted structure compared to rutile, anatase structure has two of the titanium-oxygen bonds that are much longer than the other four bonds. On the other hand, brookite has the same interatomic distance to those of rutile and anatase, but different in its O-Ti-O bond angles [5]. Figure 1.2 shows the schematic conventional unit cells for (a) anatase, (b) rutile, and (c) brookite TiO_2. Each polymorph of titanium dioxide contributes to different uses. For rutile phased TiO_2, due to its high refractive index, it is usually used in high-grade, corrosion-protective white coatings and paint, or plastics, rubber, leather, and paper. The anatase phase has great pigment and optical properties due to its electronic structure and is usually used as an optical coating. Meanwhile, the application of brookite TiO_2 is restricted mainly because it was hard to be synthesized.

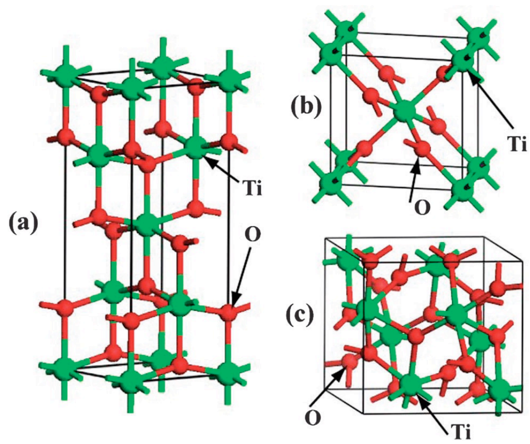

Figure 1.2: The schematic conventional unit cells for (a) anatase, (b) rutile, and (c) brookite TiO_2 [6]

Titanium dioxide is an important material because of its functional properties. For example, under certain conditions, it can absorb ultraviolet (UV) light, and is transparent to the visible light spectrum [7]. Additionally, TiO_2 is substantially less expensive than other materials and their reserve is abundant [8]. Its properties can also be altered chemically to enhance its properties, for example, through the doping process, which can provide free carriers to increase its efficiency as a photo-catalyst depending on the type of dopants used as different dopant may not have the same effect on trapping electrons and/or hole [9]. In nanomaterials, specific surface area and surface-to-volume ratio would increase as the size of nanomaterials decreases [10]. For TiO_2-based devices, high surface area from small particle size would be advantageous. Thus, the performance of TiO_2-based devices was primarily impacted by the sizes of TiO_2 materials itself, particularly at the nanometre scale.

Nanostructured materials have been extensively studied due to their potential use in fabricated micro and nanoscale devices. It has a very high aspect ratio, reduced power consumption, and higher integration densities than bulk materials. It also exhibits superior stability owing to its high crystallinity [11]. Titanium dioxide is a semiconductor material that can be shaped into various crystals. Nanowires, nanoflowers, nanorods, and nanofibers are among the many structures that have been reported in literatures as shown in Figure 1.3 [12]–[15]. Such structures exhibit novel properties that can facilitate the fabrication of novel and efficient nanoscale devices.

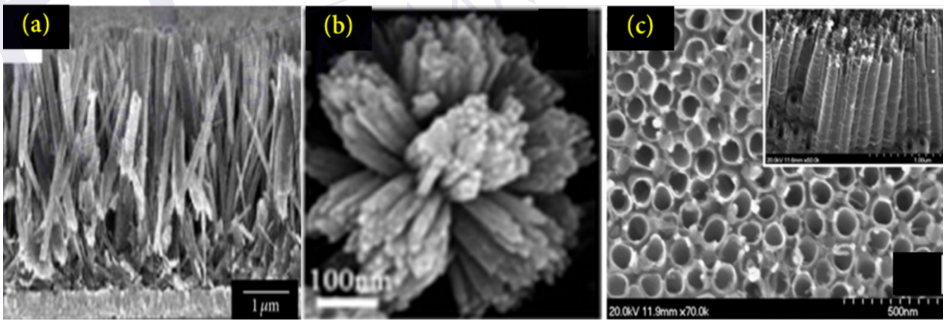

Figure 1.3: TiO_2 morphology in (a) nanorods, (b) nanoflowers, and (c) nanotubes [12], [13], [16]

Nanostructured TiO_2 has a large surface-to-volume ratio that can be used to enhance the performance of devices. As the size is reduced, devices become faster. This size reduction phenomenon also contributes to the quantum confinement phenomenon. Quantum confinement traps electrons in a small area in such a way that controlling the movement of the electrons in a particular direction becomes easier. Many investigations have focused on nanostructured TiO_2 for usage in fabricated devices, such as dye-sensitized solar cells, photocatalysts, various sensors, and LEDs. Numerous structures of TiO_2 can be produced depending on the technique used. Example of the techniques include chemical bath deposition (CBD), hydrothermal method, sol-gel method, and RF sputtering. However, solution-based techniques are preferred in producing high-quality TiO_2 at a low cost and therefore allowing the fabrication of UV sensors at minimal cost. Furthermore, using this technique, the growth of TiO_2 structure can be easily controlled via the addition of a stabilizer or surfactant. The solution-based technique has additional advantages, such as facilitating the growth of TiO_2 at low temperatures at a large-scale with simple processing methods [17].

TiO_2 has been reported to be an intrinsically n-type semiconductor due to its oxygen deficiency [18], [19]. The intrinsic n-type conductivity of TiO_2 can be enhanced by introducing elements such as boron (B), nitrogen (N), niobium (Nb), and magnesium (Mg) [20]–[22]. The doping process is done to modify an intrinsic semiconductor in order to create imperfections in the mother materials by inserting impurities in certain amounts using certain methods. Doping of TiO_2 to reduce bandgap had an early success using nitrogen as a dopant source [23]. Since then, there was an extensive study on metal and non-metal doping of TiO_2. Niobium doped TiO_2 attracted massive attention especially in photocatalysis and dye-sensitized solar cells as an anode material. After doping, the Nb element can provide excess electrons in TiO_2 conduction band. The increase of electron concentration makes the electron conductivity improved due to the positive shift of conduction band minimum (CBM) [24]. For solar cells application or self-powered photodetector, this can help suppressing recombination in TiO_2/electrolyte interface. Nb doping on TiO_2 can also help in lowering the bandgap to extend the absorption range of TiO_2 into the visible region and thus making it a visible light active catalyst under solar irradiation [25].

Other than metal doping, non-metal doping such as B, C, and N has also been extensively studied during the past years. B-doped TiO_2 has been proven to enhance the performance of solar cells [26]. This increase was mainly due to the improvement of the TiO_2 in its mobility and crystallinity. High crystallinity of B-doped TiO_2 comes from the B atom that is present in the TiO_2 matrix as a nucleus due to B^{3+} having smaller ionic radius (20 pm) than Ti^{4+} (60.5 pm), providing a good crystal growth. As for mobility, the TiO_2 nanorods crystalline structure was improved as the boron atom partially reduce the Ti^{4+}. Recently, co-doping of both metal and non-metal ions has been attracting attention to enhance its functional properties in a single deposition. For instances, a past research has shown successful co-doping of Nb and N as metal and non-metal element, respectively [27]. By using these two materials, the material was reported to have increased photocatalytic activity from N doping and conductivity from

REFERENCES

[1] T. Koutchma, "Basic Principles of UV Light Generation," in *Food Plant Safety*, First., Elsevier, 2014, pp. 3–13.

[2] M. Addamo, M. Bellardita, A. Di Paola, and L. Palmisano, "Preparation and photoactivity of nanostructured anatase, rutile and brookite TiO2 thin films.," *Chem. Commun. (Camb).*, no. 47, pp. 4943–4945, 2006, doi: 10.1039/b612172a.

[3] Y. Liao, W. Que, Q. Jia, Y. He, J. Zhang, and P. Zhong, "Controllable synthesis of brookite/anatase/rutile TiO2 nanocomposites and single-crystalline rutile nanorods array," *J. Mater. Chem.*, vol. 22, no. 16, pp. 7937–7944, 2012, doi: 10.1039/c2jm16628c.

[4] E. N. Bunting, "Phase equilibria in the systems TiO2, TiO2-SiO2 and TiO2-Al2O3," *Bur. Stand. J. Res.*, vol. 11, no. November, 1933, doi: 10.6028/jres.011.049.

[5] W. Y. C. S D Mo, "Electronic and optical properties of titanium dioxide: rutile, anatase and brookite," *Phys. Rev. B*, vol. 51, no. 19, pp. 50–59, 1995, doi: 10.1103/PhysRevB.51.13023.

[6] J. Zhang, P. Zhou, J. Liu, and J. Yu, "New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO2," *Phys. Chem. Chem. Phys.*, vol. 16, no. 38, pp. 20382–20386, 2014, doi: 10.1039/C4CP02201G.

[7] H. Yang, S. Zhu, and N. Pan, "Studying the mechanisms of titanium dioxide as ultraviolet-blocking additive for films and fabrics by an improved scheme," *J. Appl. Polym. Sci.*, vol. 92, no. 5, pp. 3201–3210, 2004, doi: 10.1002/app.20327.

[8] Y. Li, X. Lv, and J. Li, "High performance binderless TiO2 nanowire arrays electrode for lithium-ion battery," *Appl. Phys. Lett.*, vol. 95, no. 11, pp. 2009–2011, 2009, doi: 10.1063/1.3224888.

[9] X. D. Tang *et al.*, “Study of Nd3+,Pd2+,Pt4+, and Fe3+ dopant effect on photoreactivity of TiO2 nanoparticles,” *J. Biochem.*, vol. 99, no. 10, 2002.

[10] X. Chen and S. S. Mao, “Titanium Dioxide Nanomaterials : Synthesis , Properties , Modifications , and Applications,” *Chem. Rev.*, vol. 107, pp. 2891–2959, 2007.

[11] E. Comini, C. Baratto, G. Faglia, M. Ferroni, A. Vomiero, and G. Sberveglieri, “Quasi-one dimensional metal oxide semiconductors: Preparation, characterization and application as chemical sensors,” *Prog. Mater. Sci.*, vol. 54, no. 1, pp. 1–67, 2009, doi: 10.1016/j.pmatsci.2008.06.003.

[12] S. S. Mali *et al.*, “Hydrothermal synthesis of rutile TiO2 nanoflowers using Brønsted Acidic Ionic Liquid [BAIL]: Synthesis, characterization and growth mechanism,” *CrystEngComm*, vol. 14, no. 6, p. 1920, 2012, doi: 10.1039/c2ce06476f.

[13] Y. X. Zhang, G. H. Li, Y. X. Jin, Y. Zhang, J. Zhang, and L. D. Zhang, “Hydrothermal synthesis and photoluminescence of TiO 2 nanowires,” vol. 365, pp. 300–304, 2002.

[14] P. Dong, Y. Wang, B. Liu, L. Guo, Y. Huang, and S. Yin, “Applied Surface Science Effect of hydrothermal reaction time on morphology and photocatalytic activity of H 2 Ti 3 O 7 nanotubes obtained via a rapid synthesis route,” *Appl. Surf. Sci.*, vol. 258, no. 18, pp. 7052–7058, 2012, doi: 10.1016/j.apsusc.2012.03.164.

[15] J. G. Lu, P. Chang, and Z. Fan, “Quasi-one-dimensional metal oxide materials-Synthesis, properties and applications,” *Mater. Sci. Eng. R Reports*, vol. 52, no. 1–3, pp. 49–91, 2006, doi: 10.1016/j.mser.2006.04.002.

[16] P. Dong, Y. Wang, B. Liu, L. Guo, Y. Huang, and S. Yin, “Effect of hydrothermal reaction time on morphology and photocatalytic activity of H2Ti3O7 nanotubes obtained via a rapid synthesis route,” *Appl. Surf. Sci.*, vol. 258, no. 18, pp. 7052–7058, 2012, doi: 10.1016/j.apsusc.2012.03.164.

[17] A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, and A. Salleo, “Materials and applications for large area electronics: Solution-based approaches,” *Chem. Rev.*, vol. 110, no. 1, pp. 3–24, 2010, doi: 10.1021/cr900150b.

[18] L. Forro *et al.*, “High mobility n-type charge carriers in large single crystals,” *New York*, vol. 75, pp. 633–635, 1994.

[19] S. U. M. Khan, M. Al-Shahry, and W. B. Ingler, “Efficient photochemical water splitting by a chemically modified n-TiO2.,” *Science (80-.).*, vol. 297, no. 5590, pp. 2243–2245,

2002, doi: 10.1126/science.1075035.

[20] C. Zhang, Y. Jia, Y. Jing, Y. Yao, J. Ma, and J. Sun, "Effect of non-metal elements (B, C, N, F, P, S) mono-doping as anions on electronic structure of SrTiO3," *Comput. Mater. Sci.*, vol. 79, pp. 69–74, 2013, doi: 10.1016/j.commatsci.2013.06.009.

[21] S. In *et al.*, "Effective Visible Light-Activated B-Doped and B , N-Codoped TiO 2 Photocatalysts," *J. Am. Chem. Soc.*, vol. 129, pp. 13790–13791, 2007, doi: 10.1021/ja0749237.

[22] M. S. H. Al-Furjan, K. Cheng, and W. Weng, "Influences of mg doping on the electrochemical performance of TiO2 nanodots based biosensor electrodes," *Adv. Mater. Sci. Eng.*, vol. 2014, 2014, doi: 10.1155/2014/965821.

[23] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides," *Science (80-.).*, vol. 293, no. 5528, pp. 269–271, 2001, doi: 10.1126/science.1061051.

[24] H. Su *et al.*, "Electrochimica Acta The Synthesis of Nb-doped TiO 2 Nanoparticles for Improved-Performance Dye Sensitized Solar Cells," *Electrochim. Acta*, vol. 182, pp. 230–237, 2015, doi: 10.1016/j.electacta.2015.09.072.

[25] D. Y. Lee, J. H. Park, Y. H. Kim, M. H. Lee, and N. I. Cho, "Effect of Nb doping on morphology, crystal structure, optical band gap energy of TiO2thin films," *Curr. Appl. Phys.*, vol. 14, no. 3, pp. 421–427, 2014, doi: 10.1016/j.cap.2013.12.025.

[26] Y. C. Tu, H. Lim, C. Y. Chang, J. J. Shyue, and W. F. Su, "Enhancing performance of P3HT: TIO2 solar cells using doped and surface modified TiO2 nanorods," *J. Colloid Interface Sci.*, vol. 448, pp. 315–319, 2015, doi: 10.1016/j.jcis.2015.02.015.

[27] N. P. Chadwick, E. N. K. Glover, S. Sathasivam, and S. N. Basahel, "Photo-activity and Low Resistivity in N/Nb Co-doped TiO2 Thin Films by Combinatorial AACVD," *J. Mater. Chem. A*, vol. 4, no. 2, pp. 407–415, 2016.

[28] H. Wang and J. P. Lewis, "Second-generation photocatalytic materials: Anion-doped TiO2," *J. Phys. Condens. Matter*, vol. 18, no. 2, pp. 421–434, 2006, doi: 10.1088/0953-8984/18/2/006.

[29] M. Duta *et al.*, "Nb-doped TiO2 sol-gel films for CO sensing applications," *Mater. Sci. Semicond. Process.*, vol. 42, pp. 397–404, 2016, doi: 10.1016/j.mssp.2015.11.004.

[30] G. Peng *et al.*, "UV-induced SiC nanowire sensors," *J. Phys. D. Appl. Phys.*, vol. 48, no. 5, p. 055102, 2015, doi: 10.1088/0022-3727/48/5/055102.

[31] Z. Jakšić, M. Maksimović, and M. Sarajlić, "Silver–silica transparent metal structures as bandpass filters for the ultraviolet range," *J. Opt. A Pure Appl. Opt.*, vol. 7, no. 1, pp. 51–55, 2004, doi: 10.1088/1464-4258/7/1/008.

[32] E. Roduner, "Size matters: why nanomaterials are different," *Chem. Soc. Rev.*, vol. 35, no. 7, p. 583, 2006, doi: 10.1039/b502142c.

[33] M. Valden, "Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties," *Science (80-.).*, vol. 281, no. 5383, pp. 1647–1650, 1998, doi: 10.1126/science.281.5383.1647.

[34] P. Soundarrajan, K. Sankarasubramanian, T. Logu, K. Sethuraman, and K. Ramamurthi, "Growth of rutile TiO2 nanorods on TiO2 seed layer prepared using facile low cost chemical methods," *Mater. Lett.*, vol. 116, pp. 191–194, Feb. 2014, doi: 10.1016/j.matlet.2013.11.026.

[35] J. H. Kim, T. K. Yun, J. Y. Bae, and K. S. Ahn, "Enhanced carrier transport of N-doped TiO2 for photoelectrochemical cells," *Jpn. J. Appl. Phys.*, vol. 48, no. 12, 2009, doi: 10.1143/JJAP.48.120204.

[36] A. Fujishima and K. Honda, "© 1972 Nature Publishing Group," *Nature*, vol. 238, pp. 37–38, 1972.

[37] A. P. Popov, A. V Priezzhev, J. Lademann, and R. Myllylä, "TiO_2 nanoparticles as an effective UV-B radiation skin-protective compound in sunscreens," *J. Phys. D. Appl. Phys.*, vol. 38, no. 15, pp. 2564–2570, 2005, doi: 10.1088/0022-3727/38/15/006.

[38] A. J. Haider, R. H. AL– Anbari, G. R. Kadhim, and C. T. Salame, "Exploring potential Environmental applications of TiO2 Nanoparticles," *Energy Procedia*, vol. 119, pp. 332–345, 2017, doi: 10.1016/j.egypro.2017.07.117.

[39] B. A. van Driel, P. J. Kooyman, K. J. van den Berg, A. Schmidt-Ott, and J. Dik, "A quick assessment of the photocatalytic activity of TiO2 pigments - From lab to conservation studio!," *Microchem. J.*, vol. 126, pp. 162–171, 2016, doi: 10.1016/j.microc.2015.11.048.

[40] Z. Liu, X. Su, G. Hou, S. Bi, Z. Xiao, and H. Jia, "Spherical TiO2 aggregates with different building units for dye-sensitized solar cells.," *Nanoscale*, vol. 5, no. 17, pp.

8177–83, 2013, doi: 10.1039/c3nr01767b.

[41] K. Lee, A. Mazare, and P. Schmuki, “One-dimensional titanium dioxide nanomaterials: Nanotubes,” *Chem. Rev.*, vol. 114, no. 19, 2014, doi: 10.1021/cr500061m.

[42] G. E. Patil, D. D. Kajale, V. B. Gaikwad, and G. H. Jain, “Spray Pyrolysis Deposition of Nanostructured Tin Oxide Thin Films,” *ISRN Nanotechnol.*, vol. 2012, pp. 1–5, 2012, doi: 10.5402/2012/275872.

[43] A. Ranga Rao and V. Dutta, “Low-temperature synthesis of TiO2 nanoparticles and preparation of TiO2 thin films by spray deposition,” *Sol. Energy Mater. Sol. Cells*, vol. 91, no. 12, pp. 1075–1080, 2007, doi: 10.1016/j.solmat.2007.03.001.

[44] G. El Fidha *et al.*, “Physical and photocatalytic properties of sprayed Dy doped ZnO thin films under sunlight irradiation for degrading methylene blue,” *RSC Adv.*, vol. 11, no. 40, pp. 24917–24925, 2021, doi: 10.1039/d1ra03967a.

[45] X. Wang and J. Shi, “Evolution of titanium dioxide one-dimensional nanostructures from surface-reaction-limited pulsed chemical vapor deposition,” *J. Mater. Res.*, vol. 28, no. 3, pp. 270–279, 2013, doi: 10.1557/jmr.2012.356.

[46] C.-W. Wang, J.-B. Chen, L.-Q. Wang, Y.-M. Kang, D.-S. Li, and F. Zhou, “Single crystal TiO2 nanorods: Large-scale synthesis and field emission,” *Thin Solid Films*, vol. 520, no. 15, pp. 5036–5041, 2012, doi: 10.1016/j.tsf.2012.03.039.

[47] D.-S. Li *et al.*, “Aligned rutile TiO2 nanorods: Facile synthesis and field emission,” *Superlattices Microstruct.*, vol. 59, pp. 187–195, 2013, doi: 10.1016/j.spmi.2013.04.010.

[48] P. Kajitvichyanukul, J. Ananpattarachai, and S. Pongpom, “Sol-gel preparation and properties study of TiO2 thin film for photocatalytic reduction of chromium(VI) in photocatalysis process,” *Sci. Technol. Adv. Mater.*, vol. 6, no. 3-4 SPEC. ISS., pp. 352–358, 2005, doi: 10.1016/j.stam.2005.02.014.

[49] Ming Zhang, Y. Bando, and K. Wada, “Sol-gel template preparation of TiO2 nanotubes and nanorods,” *J. Mater. Sci. Lett.*, vol. 20, no. 2, pp. 167–170, 2001, doi: 10.1023/A:1006739713220.

[50] N. Venkatachalam, M. Palanichamy, and V. Murugesan, “Sol-gel preparation and characterization of nanosize TiO2: Its photocatalytic performance,” *Mater. Chem. Phys.*, vol. 104, no. 2–3, pp. 454–459, 2007, doi: 10.1016/j.matchemphys.2007.04.003.

[51] S. J. Limmer, T. P. Chou, and G. Z. Cao, "A study on the growth of TiO 2 nanorods using sol electrophoresis," *J. Mater. Sci. Mater. Electron.*, vol. 9, no. 39, pp. 895–901, 2004.

[52] D. Bokov *et al.*, "Nanomaterial by Sol-Gel Method: Synthesis and Application," *Adv. Mater. Sci. Eng.*, vol. 2021, 2021, doi: 10.1155/2021/5102014.

[53] M. Sivakumar and A. Muthupandian, *Cavitation- A Novel Energy-Efficient Technique for the Generation of Nanomaterials*. 2014.

[54] J. H. Bang and K. S. Suslick, "Applications of ultrasound to the synthesis of nanostructured materials," *Adv. Mater.*, vol. 22, no. 10, pp. 1039–1059, 2010, doi: 10.1002/adma.200904093.

[55] M. Kumar, R. S. Bishnoi, A. K. Shukla, and C. P. Jain, "Techniques for formulation of nanoemulsion drug delivery system: A review," *Prev. Nutr. Food Sci.*, vol. 24, no. 3, pp. 225–234, 2019, doi: 10.3746/pnf.2019.24.3.225.

[56] A. Hassanjani-Roshan, S. M. Kazemzadeh, M. R. Vaezi, and A. Shokuhfar, "The effect of sonication power on the sonochemical synthesis of titania nanoparticles," *J. Ceram. Process. Res.*, vol. 12, no. 3, pp. 299–303, 2011.

[57] N. Wongpisutpaisan and C. Kahattha, "Titanium Dioxide Nanostructures Synthesized by Sonochemical – hydrothermal Process," *J. Met. Mater. Miner.*, vol. 23, no. 1, pp. 19–24, 2013.

[58] K. Fujihara, A. Kumar, R. Jose, S. Ramakrishna, and S. Uchida, "Spray deposition of electrospun TiO2 nanorods for dye-sensitized solar cell," *Nanotechnology*, vol. 18, no. 365709, pp. 1–6, 2007, doi: 10.1088/0957-4484/18/36/365709.

[59] H. Zhang *et al.*, "Fabrication of highly ordered TiO2 nanorod/nanotube adjacent arrays for photoelectrochemical applications," *Langmuir*, vol. 26, no. 13, pp. 11226–11232, 2010, doi: 10.1021/la1005314.

[60] A. M. Selman and Z. Hassan, "Highly sensitive fast-response UV photodiode fabricated from rutile TiO_2 nanorod array on silicon substrate," *Sensors Actuators A Phys.*, vol. 221, pp. 15–21, Jan. 2015, doi: 10.1016/j.sna.2014.10.041.

[61] Y. Wang, L. Zhang, K. Deng, X. Chen, and Z. Zou, "Low Temperature Synthesis and Photocatalytic Activity of Rutile TiO2 Nanorod Superstructures," *J. Phys. Chem. C*, vol. 111, pp. 2709–2714, 2007, doi: 10.1021/jp066519k.

[62] S. Venkatachalam, H. Hayashi, T. Ebina, and H. Nanjo, “Preparation and Characterization of Nanostructured TiO2 Thin Films by Hydrothermal and Anodization Methods,” *Optoelectron. - Adv. Mater. Devices*, pp. 115–136, 2013, doi: 10.5772/51254.

[63] L. Dong *et al.*, “Hydrothermal growth of rutile TiO2 nanorod films on titanium substrates,” *Thin Solid Films*, vol. 519, no. 15, pp. 4634–4640, May 2011, doi: 10.1016/j.tsf.2011.01.008.

[64] Y. Li, M. Guo, M. Zhang, and X. Wang, “Hydrothermal synthesis and characterization of TiO2 nanorod arrays on glass substrates,” *Mater. Res. Bull.*, vol. 44, no. 6, pp. 1232–1237, 2009, doi: 10.1016/j.materresbull.2009.01.009.

[65] J. J. Yuan, H. D. Li, S. Y. Gao, D. D. Sang, L. a. Li, and D. Lu, “Hydrothermal synthesis, characterization and properties of TiO2 nanorods on boron-doped diamond film,” *Mater. Lett.*, vol. 64, no. 18, pp. 2012–2015, 2010, doi: 10.1016/j.matlet.2010.06.033.

[66] H.-E. Wang *et al.*, “Hydrothermal synthesis of ordered single-crystalline rutile TiO[sub 2] nanorod arrays on different substrates,” *Appl. Phys. Lett.*, vol. 96, no. 26, p. 263104, 2010, doi: 10.1063/1.3442913.

[67] M. N. Tahir *et al.*, “Facile Synthesis and Characterization of Functionalized, Monocrystalline Rutile TiO 2 Nanorods,” *Am. Chem. Soc.*, no. 21, pp. 5209–5212, 2006.

[68] S. P. Chang, R. W. Chuang, S. J. Chang, C. Y. Lu, Y. Z. Chiou, and S. F. Hsieh, “Surface HCl treatment in ZnO photoconductive sensors,” *Thin Solid Films*, vol. 517, no. 17, pp. 5050–5053, 2009, doi: 10.1016/j.tsf.2009.03.042.

[69] C. Soci, A. Zhang, X.-Y. Bao, H. Kim, Y. Lo, and D. Wang, “Nanowire Photodetectors,” *J. Nanosci. Nanotechnol.*, vol. 10, no. 3, pp. 1430–1449, 2010, doi: 10.1166/jnn.2010.2157.

[70] D. Caputo, G. de Cesare, A. Nascetti, and M. Tucci, “Innovative window layer for amorphous silicon/amorphous silicon carbide UV sensor,” *J. Non. Cryst. Solids*, vol. 352, no. 9-20 SPEC. ISS., pp. 1818–1821, 2006, doi: 10.1016/j.jnoncrysol.2005.09.052.

[71] J. D. Hwang and C. C. Lin, “Gallium nitride photoconductive ultraviolet sensor with a sputtered transparent indium-tin-oxide ohmic contact,” *Thin Solid Films*, vol. 491, no. 1–2, pp. 276–279, 2005, doi: 10.1016/j.tsf.2005.05.044.

[72] K. Hayashi *et al.*, “Temporal response of UV sensors made of highly oriented diamond films by 193 and 313 nm laser pulses,” *Diam. Relat. Mater.*, vol. 10, no. 9–10, pp. 1794–

1798, 2001, doi: 10.1016/S0925-9635(01)00451-4.

[73] C. J. Lee, C. H. Won, J. H. Lee, S. H. Hahm, and H. Park, "Selectively enhanced uv-a photoresponsivity of a gan msm uv photodetector with a step-graded alxga1−xn buffer layer," *Sensors (Switzerland)*, vol. 17, no. 7, pp. 1–9, 2017, doi: 10.3390/s17071684.

[74] A. Kusior, J. Banas, A. Trenczek-Zajac, P. Zubrzycka, A. Micek-Ilnicka, and M. Radecka, "Structural properties of TiO2nanomaterials," *J. Mol. Struct.*, vol. 1157, pp. 327–336, 2018, doi: 10.1016/j.molstruc.2017.12.064.

[75] Z. Sun, T. Liao, L. Sheng, L. Kou, J. H. Kim, and S. X. Dou, "Deliberate Design of TiO $_2$ Nanostructures towards Superior Photovoltaic Cells," *Chem. - A Eur. J.*, no. May, pp. 11357–11364, 2016, doi: 10.1002/chem.201601546.

[76] Q. Li, R. Liu, B. Zou, T. Cui, and B. Liu, "Effects of hydrothermal conditions on the morphology and phase composition of synthesized TiO 2 nanostructures," *Phys. B Phys. Condens. Matter*, vol. 445, pp. 42–47, 2014, doi: 10.1016/j.physb.2014.03.079.

[77] U. M. Nayef, K. A. Hubeatir, and Z. J. Abdulkareem, "Ultraviolet photodetector based on TiO2nanoparticles/porous silicon hetrojunction," *Optik (Stuttg).*, vol. 127, no. 5, pp. 2806–2810, 2016, doi: 10.1016/j.ijleo.2015.12.002.

[78] H. Wang *et al.*, "A high-sensitive ultraviolet photodetector composed of double-layered TiO2nanostructure and Au nanoparticles film based on Schottky junction," *Mater. Chem. Phys.*, vol. 194, pp. 42–48, 2017, doi: 10.1016/j.matchemphys.2017.03.019.

[79] N. H. Kargan, M. Aliahmad, and S. Azizi, "Detecting Ultra-Violet Radiation by Using Titanium Dioxide Nanoparticles," *Soft Nanosci. Lett.*, vol. 02, no. 03, pp. 29–33, 2012, doi: 10.4236/snl.2012.23006.

[80] C. D. Wenji Zheng Xiangcun Li, Gaohong He, Xiaoming Yan, Rui Zhao, "RSC Advances," *RSC Adv.*, no. 41, pp. 21340–21346, 2014.

[81] Y. Xie *et al.*, "High-performance self-powered UV photodetectors based on TiO2 nano-branched arrays," *Nanotechnology*, vol. 25, no. 7, 2014, doi: 10.1088/0957-4484/25/7/075202.

[82] M. Zhang, D. Li, J. Zhou, W. Chen, and S. Ruan, "Ultraviolet detector based on TiO2nanowire array-polymer hybrids with low dark current," *J. Alloys Compd.*, vol. 618, pp. 233–235, 2015, doi: 10.1016/j.jallcom.2014.07.040.

[83] G. Liu *et al.*, "Effects of growth substrates on the morphologies of TiO2nanowire arrays and the performance of assembled UV detectors," *Appl. Surf. Sci.*, vol. 315, no. 1, pp. 55–58, 2014, doi: 10.1016/j.apsusc.2014.07.115.

[84] A. Zaleska, "Doped-TiO2: A Review," *Recent Patents Eng.*, vol. 2, no. 3, pp. 157–164, 2008, doi: 10.2174/187221208786306289.

[85] S. Sato, "Photocatalytic activity of NOx-doped TiO2 in the visible light region," *Chem. Phys. Lett.*, vol. 123, no. 1–2, pp. 126–128, 1986, doi: 10.1016/0009-2614(86)87026-9.

[86] Y. C. Zhang, M. Yang, G. Zhang, and D. D. Dionysiou, "HNO3-involved one-step low temperature solvothermal synthesis of N-doped TiO2 nanocrystals for efficient photocatalytic reduction of Cr(VI) in water," *Appl. Catal. B Environ.*, vol. 142–143, pp. 249–258, 2013, doi: 10.1016/j.apcatb.2013.05.023.

[87] A. M. Czoska *et al.*, "The nature of defects in fluorine-doped TiO2," *J. Phys. Chem. C*, vol. 112, no. 24, pp. 8951–8956, 2008, doi: 10.1021/jp8004184.

[88] S. C. Padmanabhan *et al.*, "A simple sol - Gel processing for the development of high-temperature stable photoactive anatase titania," *Chem. Mater.*, vol. 19, no. 18, pp. 4474–4481, 2007, doi: 10.1021/cm070980n.

[89] P. Periyat, D. E. McCormack, S. J. Hinder, and S. C. Pillai, "One-pot synthesis of anionic (nitrogen) and cationic (sulfur) codoped high-temperature stable, visible light active, anatase Photocatalysts," *J. Phys. Chem. C*, vol. 113, no. 8, pp. 3246–3253, 2009, doi: 10.1021/jp808444y.

[90] M. B. Sarkar *et al.*, " Improved UV Photodetection by Indium Doped TiO 2 Thin Film Based Photodetector ," *J. Nanosci. Nanotechnol.*, vol. 18, no. 7, pp. 4898–4903, 2017, doi: 10.1166/jnn.2018.15295.

[91] N. Prakash *et al.*, "Effect of Erbium on the Photocatalytic Activity of TiO2/Ag Nanocomposites under Visible Light Irradiation," *ChemPhysChem*, vol. 16, no. 14, pp. 3084–3092, 2015, doi: 10.1002/cphc.201500492.

[92] Y. X. Dong, X. L. Wang, E. M. Jin, S. M. Jeong, B. Jin, and S. H. Lee, "One-step hydrothermal synthesis of Ag decorated TiO2 nanoparticles for dye-sensitized solar cell application," *Renew. Energy*, vol. 135, pp. 1207–1212, 2019, doi: 10.1016/j.renene.2018.12.062.

[93] H. Li *et al.*, "Surface plasmon resonance-enhanced solar-driven photocatalytic

performance from Ag nanoparticle-decorated self-floating porous black TiO2 foams," *Appl. Catal. B Environ.*, vol. 220, pp. 111–117, 2018, doi: 10.1016/j.apcatb.2017.08.023.

[94] Y. Cong, J. Zhang, F. Chen, and M. Anpo, "Synthesis and characterization of nitrogen-doped TiO2 nanophotocatalyst with high visible light activity," *J. Phys. Chem. C*, vol. 111, no. 19, pp. 6976–6982, 2007, doi: 10.1021/jp0685030.

[95] X. Mou, J. Wu, D. Zhang, and L. Zhang, "Improved-Performance Dye-Sensitized Solar Cells Using Nb-Doped TiO 2 Electrodes : Efficient Electron Injection and Transfer," pp. 509–515, 2010, doi: 10.1002/adfm.200901292.

[96] M. Yang *et al.*, "Improved charge transport of Nb-doped TiO2nanorods in methylammonium lead iodide bromide perovskite solar cells," *J. Mater. Chem. A*, vol. 2, no. 46, pp. 19616–19622, 2014, doi: 10.1039/c4ta02635g.

[97] Y. Liu, P. Wang, C. Wang, and Y. Ao, "Polymeric carbon nitride coated Nb-TiO2 nanorod arrays with enhanced photoelectrocatalytic activity under visible light irradiation," *Inorg. Chem. Commun.*, vol. 101, no. November 2018, pp. 113–116, 2019, doi: 10.1016/j.inoche.2018.12.017.

[98] K. C. Ok *et al.*, "Semiconducting behavior of niobium-doped titanium oxide in the amorphous state," *Appl. Phys. Lett.*, vol. 100, no. 14, 2012, doi: 10.1063/1.3698389.

[99] H. Y. Wang, H. Yang, L. Zhang, J. Chen, and B. Liu, "Niobium Doping Enhances Charge Transport in TiO2Nanorods," *ChemNanoMat*, vol. 2, no. 7, pp. 660–664, 2016, doi: 10.1002/cnma.201600035.

[100] J. Xu, Y. Ao, M. Chen, and D. Fu, "Low-temperature preparation of Boron-doped titania by hydrothermal method and its photocatalytic activity," *J. Alloys Compd.*, vol. 484, no. 1–2, pp. 73–79, 2009, doi: 10.1016/j.jallcom.2009.04.156.

[101] J. Zheng, Z. Liu, X. Liu, X. Yan, D. Li, and W. Chu, "Facile hydrothermal synthesis and characteristics of B-doped TiO 2 hybrid hollow microspheres with higher photo-catalytic activity," *J. Alloys Compd.*, vol. 509, no. 9, pp. 3771–3776, 2011, doi: 10.1016/j.jallcom.2010.12.152.

[102] Y. C. Tu, J. F. Lin, W. C. Lin, C. P. Liu, J. J. Shyue, and W. F. Su, "Improving the electron mobility of TiO 2 nanorods for enhanced efficiency of a polymer-nanoparticle solar cell," *CrystEngComm*, vol. 14, no. 14, pp. 4772–4776, 2012, doi:

10.1039/c2ce25489a.

[103] Y. Wang *et al.*, "Boron-Doped TiO 2 for Efficient Electrocatalytic N 2 Fixation to NH 3 at Ambient Conditions," *ACS Sustain. Chem. Eng.*, vol. 7, no. 1, pp. 117–122, 2019, doi: 10.1021/acssuschemeng.8b05332.

[104] W. Q. Wu *et al.*, "Hydrothermal fabrication of hierarchically anatase TiO2 nanowire arrays on FTO glass for dye-sensitized solar cells," *Sci. Rep.*, vol. 3, pp. 1–7, 2013, doi: 10.1038/srep01352.

[105] B. Liu and E. S. Aydil, "Growth of Oriented Single-Crystalline Rutile TiO Nanorods on Transparent Conducting Substrates for Dye-Sensitized Solar Cells Growth of Oriented Single-Crystalline Rutile TiO 2 Nanorods on Transparent Conducting Substrates for Dye-Sensitized Solar Cells," *Glass*, no. 9, pp. 3985–3990, 2009, doi: 10.1021/ja8078972.

[106] S. Yang, L. Gao, and S. Microstructure, "Fabrication and Characterization of Nanostructurally Flowerlike Aggregates of TiO 2 via a Surfactant-free Solution Route : Effect of Various Reaction Media," vol. 34, no. 7, pp. 1044–1045, 2005, doi: 10.1246/cl.2005.1044.

[107] S. Yang, L. Gao, and S. Microstructure, "Low-temperature Synthesis of Crystalline TiO 2 Nanorods : Mass Production Assisted by Surfactant," vol. 34, no. 7, pp. 964–965, 2005, doi: 10.1246/cl.2005.964.

[108] X. Ji, W. Liu, Y. Leng, and A. Wang, "Facile Synthesis of ZnO@TiO_2 Core-Shell Nanorod Thin Films for Dye-Sensitized Solar Cells," *J. Nanomater.*, vol. 2015, pp. 1–5, 2015, doi: 10.1155/2015/647089.

[109] W. Guo *et al.*, "Rectangular bunched rutile TiO2 nanorod arrays grown on carbon fiber for dye-sensitized solar cells.," *J. Am. Chem. Soc.*, vol. 134, no. 9, pp. 4437–41, 2012, doi: 10.1021/ja2120585.

[110] T.-D. Nguyen Phan, H.-D. Pham, T. Viet Cuong, E. Jung Kim, S. Kim, and E. Woo Shin, "A simple hydrothermal preparation of TiO2 nanomaterials using concentrated hydrochloric acid," *J. Cryst. Growth*, vol. 312, no. 1, pp. 79–85, Dec. 2009, doi: 10.1016/j.jcrysgro.2009.09.032.

[111] M. H. Mamat, "Fabrication and Characterisation of Aligned Zinc Oxide Nanorod Array-Based Ultraviolet Photoconductive Sensors," Universiti Teknologi Mara, 2013.

[112] X. Meng *et al.*, "Formation Mechanism of Rutile TiO 2 Rods on Fluorine Doped Tin Oxide Glass," *J. Nanosci. Nanotechnol.*, vol. 14, no. 11, pp. 8839–8844, 2014, doi: 10.1166/jnn.2014.10016.

[113] Y. Zhang, C. X. Harris, P. Wallenmeyer, J. Murowchick, and X. Chen, "Asymmetric lattice vibrational characteristics of rutile TiO 2 as revealed by laser power dependent raman spectroscopy," *J. Phys. Chem. C*, vol. 117, no. 45, pp. 24015–24022, 2013, doi: 10.1021/jp406948e.

[114] M. K. Ahmad *et al.*, "Raman investigation of rutile-phased TiO_2 nanorods/nanoflowers with various reaction times using one step hydrothermal method," *J. Mater. Sci. Mater. Electron.*, vol. 27, no. 8, pp. 7920–7926, 2016, doi: 10.1007/s10854-016-4783-z.

[115] J. S. Ko, N. Q. Le, D. R. Schlesinger, J. K. Johnson, and Z. Xia, "Novel niobium-doped titanium oxide towards electrochemical destruction of forever chemicals," *Sci. Rep.*, vol. 11, no. 1, pp. 1–11, 2021, doi: 10.1038/s41598-021-97596-7.

[116] S. Sugapriya, R. Sriram, and S. Lakshmi, "Effect of annealing on TiO2 nanoparticles," *Opt. - Int. J. Light Electron Opt.*, vol. 124, no. 21, pp. 4971–4975, Nov. 2013, doi: 10.1016/j.ijleo.2013.03.040.

[117] M. Gotić *et al.*, "Raman investigation of nanosized TiO2," *J. Raman Spectrosc.*, vol. 28, no. 7, pp. 555–558, 1997, doi: 10.1002/(SICI)1097-4555(199707)28:7<555::AID-JRS118>3.0.CO;2-S.

[118] G. Panchal, D. K. Shukla, R. J. Choudhary, V. R. Reddy, and D. M. Phase, "The effect of oxygen stoichiometry at the interface of epitaxial BaTiO3/La0.7Sr0.3MnO3 bilayers on its electronic and magnetic properties," *J. Appl. Phys.*, vol. 122, no. 8, 2017, doi: 10.1063/1.5000133.

[119] J.-S. Bae *et al.*, "Optical properties and Surface analysis of lithium incorporated Y2O3:Eu3+ ceramic phosphors," *J. Anal. Sci. Technol.*, vol. 1, no. 2, pp. 92–97, 2010, doi: 10.5355/jast.2010.92.

[120] Y. Yang, T. Sun, F. Ma, L. F. Huang, and Z. Zeng, "Superhydrophilic Fe3+Doped TiO2films with long-lasting antifogging performance," *ACS Appl. Mater. Interfaces*, vol. 13, no. 2, pp. 3377–3386, 2021, doi: 10.1021/acsami.0c18444.

[121] S. A. Abdullah *et al.*, "Influence of substrate annealing on inducing Ti 3+ and oxygen vacancy in TiO 2 thin films deposited via RF magnetron sputtering," *Appl. Surf. Sci.*,

vol. 462, no. August, pp. 575–582, 2018, doi: 10.1016/j.apsusc.2018.08.137.

[122] Y. Liu, H. Ran, J. Fan, X. Zhang, J. Mao, and G. Shao, "Fabrication and photovoltaic performance of niobium doped TiO 2 hierarchical microspheres with exposed {001} facets and high specific surface area," *Appl. Surf. Sci.*, vol. 410, pp. 241–248, 2017, doi: 10.1016/j.apsusc.2017.03.085.

[123] J. Yue *et al.*, "Mesoporous niobium-doped titanium dioxide films from the assembly of crystalline nanoparticles: study on the relationship between the band structure, conductivity and charge storage mechanism," *J. Mater. Chem. A*, vol. 5, no. 5, pp. 1978–1988, 2017, doi: 10.1039/c6ta06840e.

[124] Y. Pang and P. Wynblatt, "Effects of Nb Doping and Segregation on the Grain Boundary Plane Distribution in TiO 2," *J. Am. Ceram. Soc.*, vol. 671, no. 20723, pp. 666–671, 2006, doi: 10.1111/j.1551-2916.2005.00759.x.

[125] K. M. Reddy, S. V. Manorama, and A. R. Reddy, "Bandgap studies on anatase titanium dioxide nanoparticles," *Mater. Chem. Phys.*, no. 78, pp. 239–245, 2002.

[126] M. Yang, B. Ding, and J. K. Lee, "Surface electrochemical properties of niobium-doped titanium dioxide nanorods and their effect on carrier collection efficiency of dye sensitized solar cells," *J. Power Sources*, vol. 245, pp. 301–307, 2014, doi: 10.1016/j.jpowsour.2013.06.016.

[127] L. Zheng *et al.*, "Novel D-A-π-a-type organic dyes containing a ladderlike dithienocyclopentacarbazole donor for effective dye-sensitized solar cells," *ACS Omega*, vol. 2, no. 10, pp. 7048–7056, 2017, doi: 10.1021/acsomega.7b01387.

[128] C. Huang, J. Bian, and R. Q. Zhang, "Role of Cl Ion Desorption in Photocurrent Enhancement of the Annealed Rutile Single-Crystalline TiO2 Nanorod Arrays," *J. Phys. Chem. C*, vol. 121, no. 34, pp. 18892–18899, 2017, doi: 10.1021/acs.jpcc.7b04071.

[129] M. C. Mathpal, A. K. Tripathi, M. K. Singh, S. P. Gairola, S. N. Pandey, and A. Agarwal, "Effect of annealing temperature on Raman spectra of TiO2 nanoparticles," *Chem. Phys. Lett.*, vol. 555, pp. 182–186, 2013, doi: 10.1016/j.cplett.2012.10.082.

[130] Y. Li, L. Wei, R. Zhang, Y. Chen, and J. Jiao, "Annealing effect on photovoltaic performance of CdSe quantum-dots- sensitized TiO2 nanorod solar cells," *J. Nanomater.*, vol. 2012, 2012, doi: 10.1155/2012/103417.

[131] I. E. Grey, C. Li, C. M. MacRae, and L. A. Bursill, "Boron incorporation into rutile.

Phase equilibria and structure considerations," *J. Solid State Chem.*, vol. 127, no. 2, pp. 240–247, 1996, doi: 10.1006/jssc.1996.0380.

[132] Q. Zhu *et al.*, "Microsphere assembly of rutile TiO2 hierarchically hyperbranched nanorods: CdS sensitization and photovoltaic properties," *Solid State Sci.*, vol. 13, no. 6, pp. 1299–1303, Jun. 2011, doi: 10.1016/j.solidstatesciences.2011.03.025.

[133] J. Li, N. Lu, X. Quan, S. Chen, and H. Zhao, "Facile method for fabricating boron-doped TiO2 nanotube array with enhanced photoelectrocatalytic properties," *Ind. Eng. Chem. Res.*, vol. 47, no. 11, pp. 3804–3808, 2008, doi: 10.1021/ie0712028.

[134] E. Finazzi, C. Di Valentin, and G. Pacchioni, "Boron-doped anatase TiO2: Pure and hybrid DFT calculations," *J. Phys. Chem. C*, vol. 113, no. 1, pp. 220–228, 2009, doi: 10.1021/jp8072238.

[135] L. Li, F. Meng, X. Hu, L. Qiao, C. Q. Sun, and H. Tian, "TiO 2 Band Restructuring by B and P Dopants," pp. 1–14, 2016, doi: 10.1371/journal.pone.0152726.

[136] N. Feng *et al.*, "Unravelling the Efficient Photocatalytic Activity of Boron-induced Ti3+ Species in the Surface Layer of TiO2," *Sci. Rep.*, vol. 6, no. September, pp. 1–9, 2016, doi: 10.1038/srep34765.

[137] B. Hu, Q. Zhang, L. Niu, J. Liu, J. Rao, and X. Zhou, "Microsphere assembly of boron-doped Rutile TiO2 nanotubes with enhanced photoelectric performance," *J. Mater. Sci. Mater. Electron.*, vol. 26, no. 11, pp. 8915–8921, 2015, doi: 10.1007/s10854-015-3573-3.

[138] D. Zhao, Y. Yu, C. Cao, J. Wang, E. Wang, and Y. Cao, "The existing states of doped B 3+ ions on the B doped TiO 2," *Appl. Surf. Sci.*, vol. 345, pp. 67–71, 2015, doi: 10.1016/j.apsusc.2015.03.140.

[139] B. Buchholcz, E. Varga, T. Varga, K. Plank, J. Kiss, and Z. Kónya, "Structure and stability of boron doped titanate nanotubes and nanowires," *Vacuum*, vol. 138, pp. 120–124, 2017, doi: 10.1016/j.vacuum.2016.11.038.

[140] M. T. Aytekin, "Synthesis , characterization and photocatalytic activity of boron-doped titanium dioxide nanotubes," vol. 1180, pp. 676–682, 2019, doi: 10.1016/j.molstruc.2018.12.056.

[141] Y. Su, S. Han, X. Zhang, X. Chen, and L. Lei, "Preparation and visible-light-driven photoelectrocatalytic properties of boron-doped TiO 2 nanotubes," vol. 110, pp. 239–

246, 2008, doi: 10.1016/j.matchemphys.2008.01.036.

[142] S. Singh Surah, M. Vishwakarma, R. Kumar, R. Nain, S. Sirohi, and G. Kumar, "Tuning the electronic band alignment properties of TiO2 nanotubes by boron doping," *Results Phys.*, vol. 12, no. November 2018, pp. 1725–1731, 2019, doi: 10.1016/j.rinp.2019.01.081.

[143] F. Paquin, J. Rivnay, A. Salleo, N. Stingelin, and C. Silva, "Multi-phase semicrystalline microstructures drive exciton dissociation in neat plastic semiconductors," *J. Mater. Chem. C*, vol. 3, pp. 10715–10722, 2015, doi: 10.1039/b000000x.

[144] S. W. Guo XY, Xu DP, Ding ZH, "Preparation and Raman Spectrum of Rutile Single Crystal Using Floating Zone Method," *CHIN.PHYS.LETT.*, vol. 23, no. 6, p. 1645, 2006.

APPENDIX A

LIST OF PUBLICATIONS

1. S. M. Mokhtar, M.K. Ahmad, C.F. Soon, N.K.A. Hamed, and M. Shimomura, “Photovoltaic enhancement of nanostructured boron-doped rutile phase TiO2 nanorods via facile hydrothermal method,” J Mater Sci: Mater Electron, vol. 33, no. 12, pp. 9471-9482, 2022.
2. S. M. Mokhtar, M. K. Ahmad, S. Harish, N. K. A. Hamed, and M. Shimomura, “Surface chemistry and growth mechanism of highly oriented, single crystalline Nb-doped TiO2 nanorods,” CrystEngComm, vol. 22, no. 13, pp. 2380–2388, 2020.
3. S. M. Mokhtar, M. K. Ahmad, N. Nafarizal, C. F. Soon, M. H. Mamat, N. M. A. N. Ismail, A. S. Ameruddin, A. B. Suriani, M. Shimomura, K. Murakami., “High responsivity of ultraviolet sensor-based rutile-phased TiO2 nanorod arrayss using different bias voltage,” J. Aust. Ceram. Soc., vol. 56, no. 2, pp. 461–468, 2020.
4. S. M. Mokhtar, M.K. Ahmad, C.F. Soon, N. Nafarizal, A.B. Faridah, A.B. Suriani, M.H. Mamat, M. Shimomura, K. Murakami, “Fabrication and characterization of rutile-phased titanium dioxide (TiO2) nanorods arrays with various reaction times using one step hydrothermal method,” Optik (Stuttg)., vol. 154, pp. 510–515, 2018
5. N.K.A. Hamed, M.K Ahmad, N.H.H. Hairom, A.B. Faridah, M.H. Mamat, A. Mohamed, A.B. Suriani, N. Nafarizal, F.I.M Fazli, S.M Mokhtar, W.I.W Omar and M. Shimomura, “Dependence of photocatalysis on electron trapping in Ag-doped flowerlike rutile-phase TiO2 film by facile hydrothermal method”, Applied Surface Science, vol. 534, pp. 147571, 2020
6. M. K. Ahmad, S. M. Mokhtar, C. F. Soon, N. Nafarizal, A. B. Suriani, A. Mohamed, M. H. Mamat, M. F. Malek, M. Shimomura, and K. Murakami, “Raman investigation of rutile-phased TiO2 nanorods/nanoflowers with various reaction times using one step hydrothermal method,” J. Mater. Sci. Mater. Electron, 2016

LIST OF CONFERENCES PROCEEDING AND PRESENTATIONS

1. Salina Mohammad Mokhtar, Masaru Shimomura, Mohd Khairul Ahmad, Growth Study of Highly Oriented, Single-Crystalline Nb-doped TiO2 Nanorods for Enhance Carrier Transport, Abstracts of Papers, 18th Japan Surface Vacuum Society Chubu Branch Academic Lecture, Nagoya, Japan, Dec. 2019

APPENDIX B

LIST OF AWARDS

1. Best paper award for 12th Malaysia Technical Universities Conference on Engineering and Technology, November 2021

APPENDIX C

VITA

Salina was born in Kuala Lumpur, Malaysia, on August 26, 1991. They attended elementary school in Sekolah Kebangsaan Labohan Dagang, and graduated from Sekolah Menengah Kebangsaan Banting in December 2008. Following April, they attended Kolej Matrikulasi Pulau Pinang as preparation before enrolling to Universiti Tun Hussein Onn Malaysia and received the degree of Bachelor of Electronic (Microelectronic) Engineering in August 2014. In April 2015, they started Master of Electrical Engineering from the same university and graduated in September 2017. They attended Shizuoka University in October 2017 and received Doctor of Engineering in Optical Electronics and Nanostructure Science in April 2021.