

PROPOSAL FOR HYDROTHERMAL TECHNIQUE FOR METAL OXIDE NANOMATERIAL SYNTHESIS: THE CASE OF ZnO AND TiO₂

Salisu I. Kunya¹, Yunusa Abdu², Mohd Kamarulzaki Mustafa³ and Mohd Khairul Ahmad⁴

¹Department of Science laboratory Technology, Jigawa State Polytechnics, Dutse, Nigeria; Department of Physics, Faculty of Physical Sciences, College of Natural and Pharmaceutical Sciences, Bayero University, Kano, Nigeria; Department of Physics and Chemistry, Faculty of Applied Sciences and Technology, Universiti Tun Hussein Onn Malaysia (UTHM), Kampus Pagoh, Jalan Panchor 84000 Muar, Johor, Malaysia

²Department of Physics, Faculty of Physical Sciences, College of Natural and Pharmaceutical Sciences, Bayero University, Kano, Nigeria

³Department of Physics and Chemistry, Faculty of Applied Sciences and Technology, Universiti Tun Hussein Onn Malaysia (UTHM), Kampus Pagoh, Jalan Panchor 84000 Muar, Johor, Malaysia

⁴Microelectronic and Nanotechnology–Shamsuddin Research Centre (MiNT-SRC), Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia (UTHM), Parit Raja, Batu Pahat Johor, 86400, Malaysia

Corresponding Author: Salisu I. Kunya,

E-mail: salisukunya2016@gmail.com

ABSTRACT

Solar cells based on dye synthesis have gained traction in the energy generation fields. As a result, this study emphasizes the importance of the hydrothermal method for the synthesis of nanomaterials (ZnO and TiO₂) in a closed system under controlled conditions for DSSC applications. The method is straightforward, compact, less dangerous, and economical. The hydrothermal method has several pluses over traditional material handling techniques including the ability to crystallize materials, grow crystals, and process a diverse range of materials, fine particles of well-ordered size and morphology. A detailed explanation of reaction media, dye synthesis solar cells, nanomaterials, and a general approach to nanomaterial synthesis were also included in the study

Keywords: Hydrothermal, ZnO, TiO₂, Top-down, and Bottom-up technique.

1. INTRODUCTION

The foundation of a material scientist is synthesis. It is the use of non-natural chemical reactions to produce the desired product. When certain conditions are met, one or more reagents will undergo a transformation. There are numerous nanomaterial synthesis techniques for dye synthesis solar cell (DSSC) applications, one of which is hydrothermal. Hydrothermal nanomaterial synthesis is essentially a solution reaction-based approach [1]. The phrase "hydrothermal" originated from "hydro" which implies water, and "thermal" which implies heat and summarizes the consequence of water at enhanced pressure and temperature [2] A hydrothermal reaction is any combined chemical reaction that occurs in a covered container with an aqueous solvent above ambient temperature and at a pressure greater than one atm. [3]. The hydrothermal method is most normally used in a closed container under pressure called Autoclave. Metal oxides, hydroxides, sulfides, carbonates, phosphates, nitrides, and selenides have the

potential to be prepared using these techniques for a wide range of technological applications such as electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical, biophotonics, and so on. [4]. One of the key benefits of the hydrothermal chemical method over the others is that it yields uniform crystallite materials, has greater diffusivity, low viscosity, and mass transport consumes less energy, has a moderate reaction time, and is a secure option with no natural dangers because it is a closed system preparation method. The method can also be used to create nanomaterials like nanoparticles, nanorods, nanotubes, hollow nanospheres, and graphene nanosheets [5], [6].

2. REACTION MEDIA OF HYDROTHERMAL METHOD

Water, a compound with the structural formula H₂O, is among the most vital resources found in abundance. Water can act as a reaction medium or a solvent in a hydrothermal reaction. Water behaves differently under hydrothermal conditions than it

does under normal conditions. The process of hydrothermal synthesis takes place below the supercritical temperature of water (374°C).[7].

Under supercritical conditions, the dielectric constant and solubility of many compounds change dramatically.

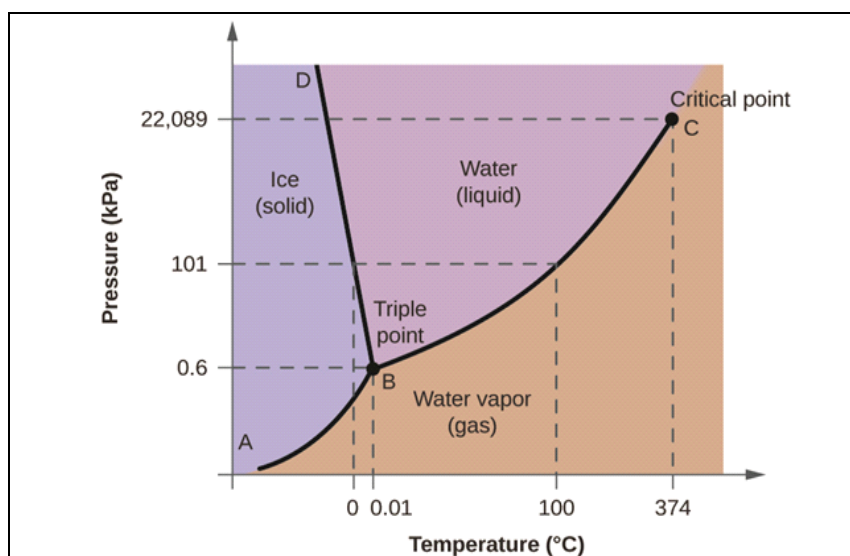


Figure 1. Phase diagram of water

Figure 1 depicts the regions of three distinct phases: solid, liquid, and vapor. Over the range of temperature associated with its corresponding area, each phase will maintain equilibrium. Furthermore, the curves on the plot (labeled AB, CB, and DB) are phase boundaries; at any spot of any of these curves, the two components on either side of the line are in balance. As illustrated in Figure, all the curves cross at a common point labeled B. This appears to imply that at this spot, all three phases are in equilibrium with one another. Commonly, varying the reaction parameters of the system, may result in change of the morphology, microstructure, and phase composition of materials [8]. Yan et al. [9] revealed that increasing the temperature and pressure of the reaction media results in:

1. An increase in the ionization constant of water, favors an increase in the rate of hydrolysis and ionic reaction.
2. Increased crystal structure formation due to increased mobility of ions and molecules in solution as a result of decreased viscosity and surface tension of water
3. A decrease in the dielectric constant affects the capability and behavior of water as a solvent.

3. DYE-SENSITIZED SOLAR CELL (DSSC)

A DSSC is a photochemical solar cell that alters sunlight into energy employing an electrolyte as a medium [10]. The dye-sensitized solar cell (DSSC) is a revolutionary device that has the potential to replace the existing solid-state p-n junction type.

Making a DSSC is less difficult than creating customary cells. When compared to ordinary solar cells that use photovoltaic effect on semiconductor junctions where light absorption and electric charge separation processes occur concurrently, DSSC however has different processes

Light absorption was accomplished through the use of a light-sensitive molecule identified as a dye, which was anchored to the semiconductor material. Thus, the basic design of a photoanode necessitates the use of mesoporous nanomaterials with wider internal surface regions, which aid in dye absorption while also providing a large interface with the whole conducting electrolyte. [11]. When the dye absorbs light, its molecular energy is excited, boosting electron injection into the semiconductor material, which then facilitates electron transfer to the conductive glass. Meanwhile, the excitation hole was transferred from dye to electrolyte and then to the other conductive glass as a counter electrode [12].

One of the most important facts about DSSCs is that they are less expensive to manufacture; for example, the dye proposed in the literature for absorbing light could be natural or artificial [13]. Natural dyes are derived from countless plant parts; they are, however, less stable and effective than artificial dyes. Furthermore, several companies (Dyesol, G24i, Sony, Sharp, and Toyota, and so on) have accepted the task of conveying DSSC technology "from the lab to the fab"[14].

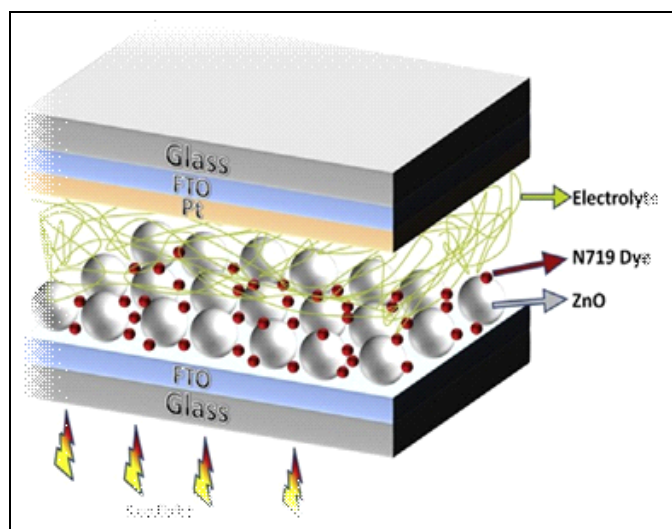


Figure 2. Dye synthesis solar cell structure

4. OVERVIEW OF NANOMATERIALS

Nanoscience and technology are modernization in the study of materials with sizes extending from a little nanometer to hundreds of nanometers. Nanomaterials and nanostructures have newly played a fundamental role in applications such as environment, electronics, optoelectronic, photovoltaic, photocatalytic, sensing devices, and health [15]. Nanomaterials emanate in a variety of shapes and sizes, including nanoparticles, nanowires, nanotubes, and nanobelts. Due to

various unique properties, nanomaterials have gotten a lot of devotion and have been thoroughly scrutinized for applications in DSSC. The two techniques used to prepare nanomaterials are: The top-down technique and the bottom-up technique

4.1 The top-down technique; is a method of reducing the size of bulk materials [16]. This synthesis route entails the application of physical ways (such as crushing, milling, sputtering, and grinding strategies) to break bulk materials into tiny ones.

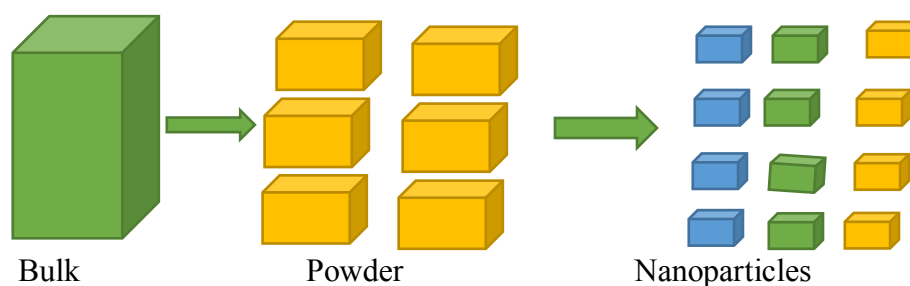


Figure 3. Top-down approach

4.2 Bottom-up approach; in this style, materials are fused atom by atom, molecule by molecule, or cluster by cluster to yield large mass. Most nanoscale materials are more commonly prepared using this method. The method results in enhanced particle size distribution and morphology. The sol-gel method, chemical vapor deposition, and

hydrothermal method are illustrations of this technique. However, in terms of environmental impact and operational costs for greater yield, the hydrothermal method is the preferred choice considering that it is simple, cheap, and efficient for getting higher purified brands in both phases and morphology. [17].

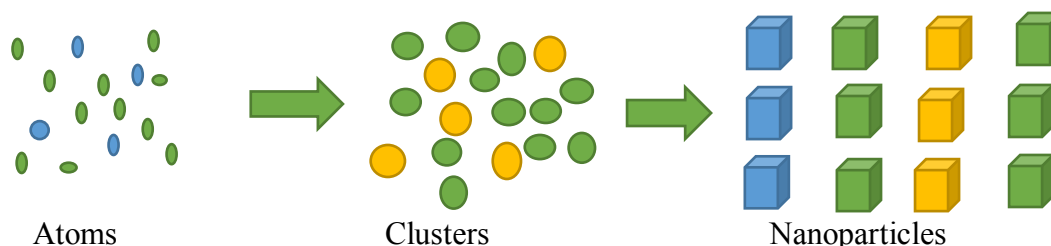


Figure 4. Bottom-up approach

5. METAL OXIDE NANOMATERIAL

The image of the materials in 1-100nm distinguishes them from whole materials in terms of physical, chemical, and catalytic characteristics. Metal oxide nanomaterials have shown promise in electronics, energy, environmental remediation, biomedical applications, and catalyst [18]. The central focus of DSSCs photoanodes is semiconducting nanostructured films. The photoanode supports the sensitizer while also transporting photogenerated particles from the dye to the external circuit. [19]. Metal oxide in photoanodes must be simple to make, stable, low in cost, and good for the environment. [20]. Furthermore, the semiconductor's band gap should be more than 3 eV, such as (TiO₂ and ZnO) coated over transparent conducting glass to permit light to pass straightforwardly through the semiconductor [14], and to enable easier charge transfer from the excited state of the dye to the semiconducting metal oxides (SMOs), the SMOs ought to be mesoporous.

5.1 Zinc oxide nanomaterials

ZnO is a multifunctional material with semiconducting, magnetic, optical, and electronic properties [21]. It has the same energy band structure and physical properties as TiO₂, but its electron mobility is 2-3 orders of magnitude higher. As a result, ZnO should have quick conduction and lower recombination. [22]. ZnO nanoparticles have several advantages over other metal oxides, together with superior elemental and thermal stability, strength, as well as prolong life [23]. The reliability of DSSCs made of ZnO photoanodes is currently around eight percent [24], [25]. Previous research advocates that the morphology of ZnO nanostructures is strongly inclined by the synthesis route and the process environment [26]. As precursors, diverse zinc salts such as zinc acetate dehydrate, zinc nitrate hexahydrate, zinc sulfate, and zinc chloride was used to create Nanostructures. [27], [28]. Photoanode beam dispersion and charge transfer attributes can be improved by changing the material's morphology. According to [29], their findings show that hydrothermal temperature has an influence on the morphology of nanorods, which has an impact on device performance. The efficiency of the ZnO nanorods base cell synthesized at 120°C, is 2.08%, which outperforms the effectiveness of standard ZnO DSSC (1.19%). Using the same amount of zinc nitrate hexahydrate and

hexamethylenetetramine, Song et al. [30] Synthesized ZnO NRs in deionized (DI) water for 4 hours at 92°C. Their results indicated an overall PCE of 4.8%.

Polsongkram et al. [31], use hydrothermal techniques at different temperatures to grow ZnO nanorods; the analysis shows that the film is hexagonal, and the morphology, ordering, and width of ZnO nanorods can be monitored by reactant concentration and temperature. Esgin et al. [32], investigates the effects of introducing copper at various ratios and times of adsorption on the ZnO DSSC. The effectiveness of 2.03 percent in DSSC was achieved when the photoanode was made with 0.1 percent and then dipped in dye solution for 60 minutes. This demonstrated that DSSC efficiency with a Cu-doped ZnO photoanode increased by twenty percent and dye adsorption time was reduced by 3 times. Pujiarti et al. [33], presents the results of hydrothermal growth of ZnO nanorods with two unlike solvents (isopropanol (P) and methoxy (Q)). ZnO nanorod grown using P as a solvent outperformed seed solution Q in terms of photovoltaic performance. The best efficiency of 1.8 percent was achieved with a 0.045 m radius ZnO nanorod in P. As a result, a smaller ZnO nanorod radius has a larger surface area, which boosts the overall quantity of dye glued to the ZnO nanorod and strengthens the output energy

5.2 Titanium dioxide nanomaterials

Titanium dioxide is a transition metal oxide (TMO) semiconductor of wide band gap (3.0 - 3.21 eV) [34]. It is an odorless, brilliantly white powder [35], and it is honestly abundant in nature [36], under normal conditions the compound is hydrophobic in nature [16]. It became revealed for the first time in 1795.[37]. The commercial production of the compound was started way back in 1920s [38]. TiO₂ plays a role in DSSCs by trapping electrons from dye oxidation caused by sunlight absorption and conveying these electrons over the conduction band of the film to the conductive glass and then through the external circuit [39]. TiO₂ nanorod and nanotube groups have a lesser recombination rate for agitated electron-hole pairs and faster electron passage than TiO₂ nanoparticles. As a result, better efficiency could be obtained when TiO₂ nanorods are used in dye-sensitized solar cells [40]. Titanium dioxide photoanode has been extensively researched as a critical component of DSSC owing to its

obtainability, ease of making, and biocompatibility. The issue with TiO₂ is its inability to absorb light (It can only capture in the Ultraviolet region.) and its low electron mobility. The band gap is altered by fixing with the appropriate cation/ anion. This increases absorption capacity beyond the UV region, resulting in a change in electrical and optical properties. [41]. The hydrothermal synthesis of TiO₂ is an appropriate synthetic approach due to advantages such as proper crystallization temperature, environmental friendliness, the flexibility of reactions, lower power consumption, and cheapness [42]. Numerous studies on the TiO₂ properties under illumination have been published. Gomathi et al. [42], synthesis rutile phase of TiO₂ nanowire for solar cell applications. The DSSC output achieved the highest efficiency of 5.1%. Anajafi et al. [43], had grown TiO₂ hydrothermally at autoclaving pH ranging from 8.0 to 12.0. It was discovered that the energy output was higher in the pH state of 10.0. In this state, the cell's photovoltaic characteristics are $I_{sc} = 15.25\text{mA}/\text{cm}^2$, $V_{oc} = 740\text{mV}$, $FF = 0.6$, and $\eta = 6.8\%$. Dong et al. [44], used the hydrothermal method to create Ag-TiO₂ nanoparticles for DSSC. The efficiency of DSSC made from 0.1M Ag-decorated (Ag_{0.1}-TiO₂) nanoparticle was 6.44%, which was superior to the TiO₂-DSSC (of 5.05%). When compared to undoped TiO₂ particles, this was due to higher visible light absorption and a wider absorption edge. Moreover, under different hydrothermal reactions, a one-step process was employed in the synthesis of rutile TiO₂ nanorods and nanoflowers structure. The following observation were reported $I_{sc} = 0.7097\text{V}$, and $\eta = 3.42\%$ [45]. Sánchez-García et al. [46], reported on the hydrothermal process used to synthesize anatase nanoparticles. The finding were given as T = 200 °C and P = 54 atm, and yielding a 5.63% efficiency

6. METHODOLOGY

The goal of this research is to better comprehend the hydrothermal technique used to create ZnO and TiO₂ nanomaterials. The hydrothermal process entailed relating precursors and right reagents in a water as solvent to allow the synthesis of a crystalline nanostructure with a suitable ratio. Moving the mixture into a sealed autoclave and heated in an oven at a precise temperature, time, and pressure is part of the procedure. The temperature at the boiling point of water can be

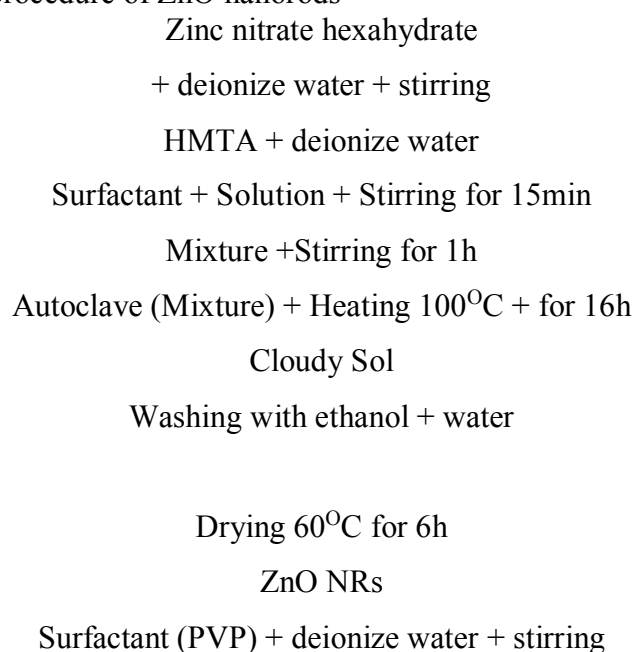
raised, allowing the vapor to grow into saturated. The heating rate and quantity of solution added to the autoclave have the greatest influence on the pressure that is formed. [17]. The following relationship has been used for regulating the concentration of the solution [47]:

$$C = \left(\frac{m}{V}\right) \times \left(\frac{1}{MV}\right) \quad (1)$$

C is the concentration, m is mass, V is the capacity of solvent, and MV is the molecular weight in g/mol. Facts of the performance procedure are presented below

6.1 Synthesis of ZnO nanorods

Separately, aqueous solutions of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) are prepared for 30 minutes with constant stirring. A PVP surfactant solution is prepared in 30 mL of water. The surfactant and zinc salt solution are mixed and constantly stirred for 15 minutes. Drops of HMTA solution are introduced to the above-prepared solution, and the mixture is stirred for 1 hour at room temperature. As a result, a cloudy solution evolved. The mixture is then transferred into a Teflon-lined autoclave. After that, place the autoclave in a 100°C oven for 16 hours. After the specified time, the mixture turned to white precipitates. Finally, the mixture is washed with ethanol, later by water, and dried in an oven at 60°C for 6 hours. The procedure is repeated for different temperatures of hydrothermal synthesis of ZnO NRs [29]. Figure 4 below is a flow chart that explains the synthesis procedure of ZnO nanorods



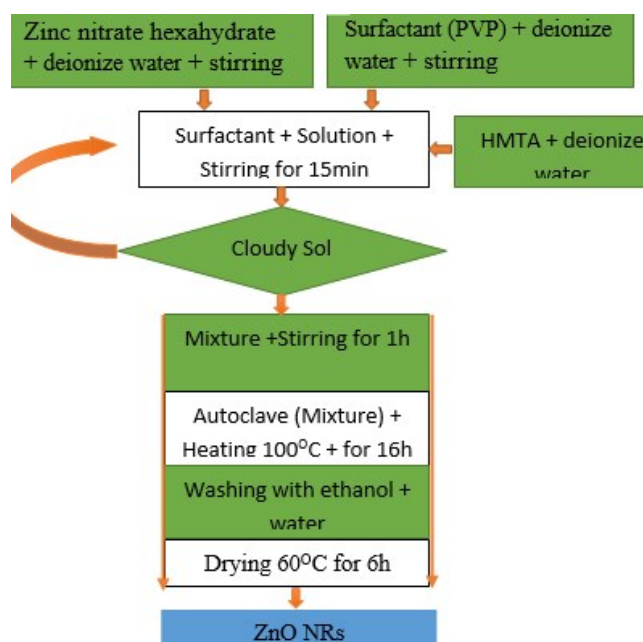


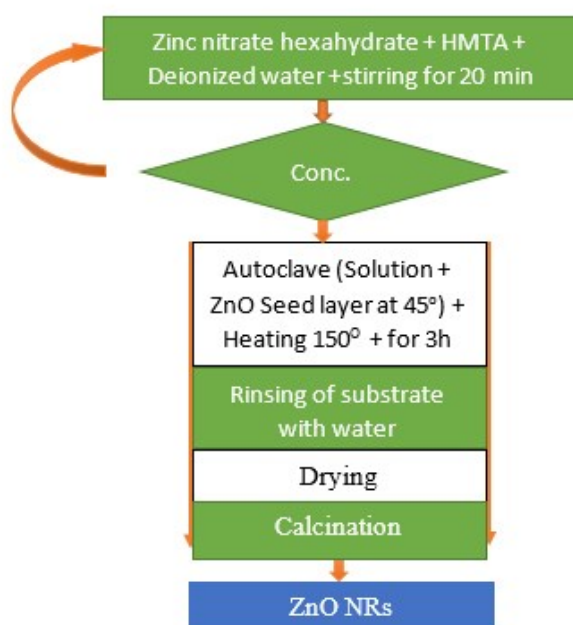
Figure 5. Illustration of ZnO NRs synthesis

6.2 Synthesis of ZnO nanorods on seeded substrate

The creation of ZnO nanorods using hydrothermal method is as follows. Initially, prepare an appropriate concentration of growth mixture solution by dissolving zinc nitrate hexahydrate and hexamethylenetetramine in a beaker filled with 100mL deionized water. The resulting solution is agitated for 20 min to create a uniform mixture. The concoction is ready to transfer into an autoclave with a ZnO seed layer at 45° to the wall. The autoclave is then placed in an oven and heated for 4

hours at 120°C. Finally, the finished product is detached from the device and cleaned with deionized water and desiccated

- Zinc nitrate hexahydrate + HMTA + Deionized water +stirring for 20 min
- Autoclave (Solution + ZnO Seed layer at 45°) + Heating 150° + for 3h
- Conc.
- Rinsing of substrate with water
- Drying
- ZnO NRs
- Calcination



6. Illustration of ZnO NRs synthesis

6.3. Synthesis of TiO₂ nanorods

The hydrothermal route of synthesis of TiO₂ is depicted in Figure 1. To get a homogeneous solution estimates a quantity of titanium tetra isopropoxide, dissolve it into 100 mL of deionized water and stir for 3 hours. Drop by drop, a sodium hydroxide solution NaOH is added to this solution, then stir for 30 minutes until white precipitate forms. Next, pour the amount of NaOH into the mixture until the pH is between 7 and 9. Finally, the prepared solution carries over to a stainless-steel autoclave lined with Teflon, allowing it to stand for 12 hours at 150 °C. The precipitate is centrifuged many times with pure liquids and ethanol to remove

unwanted materials before being desiccated at 80°C for 1 hour. After drying, the sample is allowed to stay for 1 hour in a furnace set at 400°C [48]

Titanium tetra isopropoxide + deionized water + stirring for 3h
 Sodium hydroxide + deionize water
 Drops of NaOH + Solution + Stirring for 30min
 Autoclave (Mixture) + Heating 150^o + for 12h
 Washing with ethanol + water
 p H (7-9)
 Centrifugation
 Drying 80^oC for 1h
 Annealing 400^oC for 1h
 TiO₂

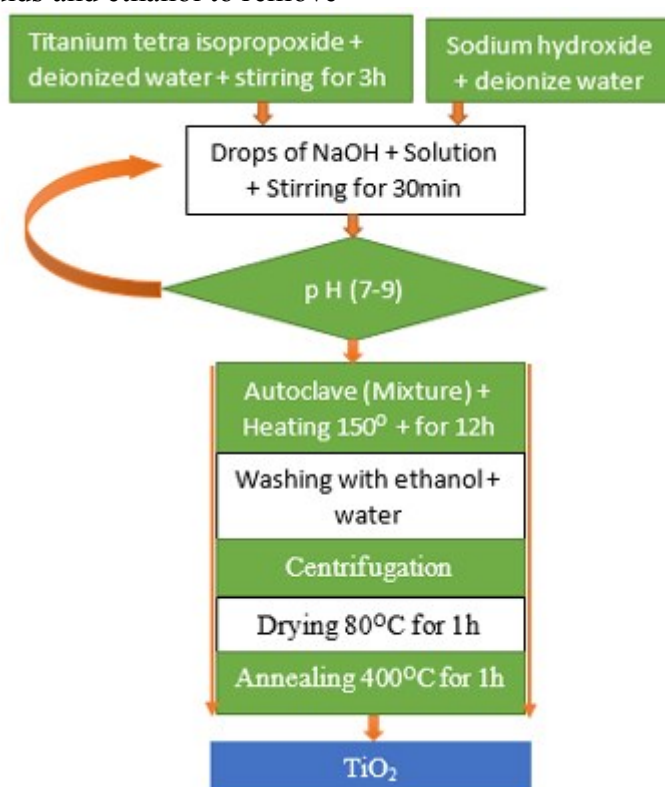


Figure 7. Illustration of TiO₂ synthesis

7. CONCLUSION

The foundation for developing dye synthesis solar cells is synthesis. In this paper, we proposed a hydrothermal method for synthesizing ZnO and TiO₂. The technique demonstrated the ability to produce ZnO and TiO₂ nanomaterials with the

required properties for DSSC formation. The chosen method is simple to use, the reactions take place primarily in a closed system and are monitorable to produce well-crystalline ZnO and TiO₂.

REFERENCES

1. M. H. Razali, N. A. Ismail, and K. A. M. Amin, "Study on phase transition of hydrothermally synthesized 1-D titanate into titania (TiO₂) as a potential nanobiomaterials," *Int. J. Appl. Chem.*, vol. 12, no. 4, pp. 629–634, 2016.
2. M. Yoshimura and K. Byrappa, "Hydrothermal processing of materials: Past, present and future," *J. Mater. Sci.*, vol. 43, no. 7, pp. 2085–2103, 2008, doi: 10.1007/s10853-007-1853-x.

3. Y. Wang, Y. He, Q. Lai, and M. Fan, "Review of the progress in preparing nano TiO₂: An important environmental engineering material," *J. Environ. Sci. (China)*, vol. 26, no. 11, pp. 2139–2177, 2014, doi: 10.1016/j.jes.2014.09.023.
4. S. R. Brintha and M. Ajitha, "Synthesis and characterization of ZnO nanoparticles via aqueous solution, sol-gel and hydrothermal methods," *IOSR J. Appl. Chem.*, vol. 8, no. 11, pp. 66–72, 2015, doi: 10.9790/5736-081116672.
5. Y. X. Gan, A. H. Jayatissa, Z. Yu, X. Chen, and M. Li, "Hydrothermal Synthesis of Nanomaterials," *J. Nanomater.*, vol. 2020, 2020, doi: 10.1155/2020/8917013.
6. S. Ugemuge and S. J. Dhoble, "Perspectives of hydrothermal synthesis of fluorides for luminescence applications: Fluorides phosphors for luminescence," *Emerg. Synth. Tech. Lumin. Mater.*, pp. 277–303, 2018, doi: 10.4018/978-1-5225-5170-6.ch008.
7. S. Nayak, A. Chaudhari, and B. Vaidhun, "A review of zinc oxide nanoparticles: an evaluation of their synthesis, characterization and ameliorative properties for use in the food, pharmaceutical and cosmetic industries," *J. Excipients Food Chem.*, vol. 11, no. December, pp. 79–92, 2020.
8. A. Info, "Effect of Calcination Temperature on the Physical Properties and Photocatalytic Activity of TiO₂ Nanotubes Synthesized by Simple Hydrothermal Method," *Aust. J. Basic Appl. Sci.*, vol. 9, no. 12, pp. 139–143, 2015.
9. G. Yang and S. J. Park, "Conventional and microwave hydrothermal synthesis and application of functional materials: A review," *Materials (Basel)*, vol. 12, no. 7, 2019, doi: 10.3390/ma12071177.
10. E. Mirabi, F. Akrami Abarghuie, and R. Arazi, "Integration of buildings with third-generation photovoltaic solar cells: A review," *Clean Energy*, vol. 5, no. 3, pp. 505–526, 2021, doi: 10.1093/ce/zkab031.
11. V. Dutta, "Spray deposited ZnO nanostructured layers for dye sensitized solar cells," *Energy Procedia*, vol. 3, pp. 58–62, 2011, doi: 10.1016/j.egypro.2011.01.010.
12. G. P. Smestad, "Education and solar conversion: Demonstrating electron transfer," *Sol. Energy Mater. Sol. Cells*, vol. 55, no. 1–2, pp. 157–178, 1998, doi: 10.1016/S0927-0248(98)00056-7.
13. A. Parisi, R. Pernice, A. Andò, A. C. Cino, V. Franzitta, and A. C. Busacca, "Electro-optical characterization of ruthenium-based dye sensitized solar cells: A study of light soaking, ageing and temperature effects," *Optik (Stuttg.)*, vol. 135, pp. 227–237, Apr. 2017, doi: 10.1016/j.ijleo.2017.01.100.
14. A. Mboniyirivuze *et al.*, "Titanium Dioxide Nanoparticles Biosynthesis for Dye Sensitized Solar Cells application: Review," *Phys. Mater. Chem.*, vol. 3, no. 1, pp. 12–17, 2015, doi: 10.12691/pmc-3-1-3.
15. Q. Zhang, C. S. Dandeneau, X. Zhou, and C. Cao, "ZnO nanostructures for dye-sensitized solar cells," *Adv. Mater.*, vol. 21, no. 41, pp. 4087–4108, 2009, doi: 10.1002/adma.200803827.
16. V. Verma, M. Al-Dossari, J. Singh, M. Rawat, M. G. M. Kordy, and M. Shaban, "A Review on Green Synthesis of TiO₂ NPs: Synthesis and Applications in Photocatalysis and Antimicrobial," *Polymers (Basel)*, vol. 14, no. 7, 2022, doi: 10.3390/polym14071444.
17. M. H. Razali, A. F. Mohd Noor, A. R. Mohamed, and S. Sreekantan, "Morphological and structural studies of titanate and titania nanostructured materials obtained after heat treatments of hydrothermally produced layered titanate," *J. Nanomater.*, vol. 2012, 2012, doi: 10.1155/2012/962073.
18. S. H. Gebre and M. G. Sendeku, "New frontiers in the biosynthesis of metal oxide nanoparticles and their environmental applications: an overview," *SN Appl. Sci.*, vol. 1, no. 8, pp. 1–28, 2019, doi: 10.1007/s42452-019-0931-4.
19. C. Cavallo, F. Di Pascasio, A. Latini, M. Bonomo, and D. Dini, "Nanostructured Semiconductor Materials for Dye-Sensitized Solar Cells," *J. Nanomater.*, vol. 2017, 2017, doi: 10.1155/2017/5323164.
20. J. Maçaira, L. Andrade, and A. Mendes, "Review on nanostructured photoelectrodes for next generation dye-sensitized solar cells," *Renew. Sustain. Energy Rev.*, vol. 27, no. 2013, pp. 334–349, 2013, doi: 10.1016/j.rser.2013.07.011.
21. S. Janet Priscilla, V. Andria Judi, R. Daniel, and K. Sivaji, "Effects of chromium doping on the electrical properties of ZnO nanoparticles," *Emerg. Sci. J.*, vol. 4, no. 2, pp. 82–88, 2020.

- doi: 10.28991/esj-2020-01212.
22. S. H. Ko *et al.*, "Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell," *Nano Lett.*, vol. 11, no. 2, pp. 666–671, 2011, doi: 10.1021/nl1037962.
 23. E. Y. Shaba, J. O. Jacob, J. O. Tijani, and M. A. T. Suleiman, *A critical review of synthesis parameters affecting the properties of zinc oxide nanoparticle and its application in wastewater treatment*, vol. 11, no. 2. Springer International Publishing, 2021. doi: 10.1007/s13201-021-01370-z.
 24. Y. He, J. Hu, and Y. Xie, "High-efficiency dye-sensitized solar cells of up to 8.03% by air plasma treatment of ZnO nanostructures," *Chem. Commun.*, vol. 51, no. 90, pp. 16229–16232, 2015, doi: 10.1039/c5cc04567c.
 25. D. Kishore Kumar *et al.*, "Functionalized metal oxide nanoparticles for efficient dye-sensitized solar cells (DSSCs): A review," *Mater. Sci. Energy Technol.*, vol. 3, pp. 472–481, 2020, doi: 10.1016/j.mset.2020.03.003.
 26. N. Islavath, D. Das, S. V. Joshi, and E. Ramasamy, "Seed layer-assisted low temperature solution growth of 3D ZnO nanowall architecture for hybrid solar cells," *Mater. Des.*, vol. 116, pp. 219–226, 2017, doi: 10.1016/j.matdes.2016.12.018.
 27. M. J. Sierra, A. P. Herrera, and K. A. Ojeda, "Synthesis of zinc oxide nanoparticles from mango and soursop leaf extracts," *Contemp. Eng. Sci.*, vol. 11, no. 8, pp. 395–403, 2018, doi: 10.12988/ces.2018.8228.
 28. E. J. Canto-Aguilar *et al.*, "ZnO-based dye-sensitized solar cells: Effects of redox couple and dye aggregation," *Electrochim. Acta*, vol. 258, pp. 396–404, 2017, doi: 10.1016/j.electacta.2017.11.075.
 29. M. Sufyan, U. Mehmood, Y. Qayyum Gill, R. Nazar, and A. Ul Haq Khan, "Hydrothermally synthesize zinc oxide (ZnO) nanorods as an effective photoanode material for third-generation Dye-sensitized solar cells (DSSCs)," *Mater. Lett.*, vol. 297, p. 130017, 2021, doi: 10.1016/j.matlet.2021.130017.
 30. H. Song *et al.*, "Fabrication of glass-free photoelectrodes for dye-sensitized solar cells (DSSCs) by transfer method using ZnO nanorods sacrificial layer," *Mater. Lett.*, vol. 132, pp. 27–30, 2014, doi: 10.1016/j.matlet.2014.06.032.
 31. D. Polsongkram *et al.*, "Effect of synthesis conditions on the growth of ZnO nanorods via hydrothermal method," *Phys. B Condens. Matter*, vol. 403, no. 19–20, pp. 3713–3717, 2008, doi: 10.1016/j.physb.2008.06.020.
 32. H. Esgin, Y. Caglar, and M. Caglar, "Photovoltaic performance and physical characterization of Cu doped ZnO nanopowders as photoanode for DSSC," *J. Alloys Compd.*, vol. 890, p. 161848, 2021, doi: 10.1016/j.jallcom.2021.161848.
 33. H. Pujiarti, N. A. Astarini, M. Diantoro, M. S. Aziz, and R. Hidayat, "Performance of Dye Sensitized Solar Cells (DSSCs) with ZnO Nanorod Electrode in Different Seed Solution," *JPSE (Journal Phys. Sci. Eng.)*, vol. 6, no. 2, pp. 77–82, 2021, doi: 10.17977/um024v6i22021p077.
 34. D. Reyes-Coronado, G. Rodríguez-Gattorno, M. E. Espinosa-Pesqueira, C. Cab, R. De Coss, and G. Oskam, "Phase-pure TiO₂ nanoparticles: Anatase, brookite and rutile," *Nanotechnology*, vol. 19, no. 14, 2008, doi: 10.1088/0957-4484/19/14/145605.
 35. A. J. Haider, Z. N. Jameel, and I. H. M. Al-Hussaini, "Review on: Titanium dioxide applications," *Energy Procedia*, vol. 157, pp. 17–29, 2019, doi: 10.1016/j.egypro.2018.11.159.
 36. F. I. M. Fazli *et al.*, "Dye-sensitized solar Cell using pure anatase TiO₂ annealed at different temperatures," *Optik (Stuttg.)*, vol. 140, pp. 1063–1068, 2017, doi: 10.1016/j.ijleo.2017.04.027.
 37. A. Tiwari, A. Shukla, D. Tiwari, S. S. Choi, H. G. Shin, and S. M. Lee, "Titanium dioxide nanomaterials and its derivatives in the remediation of water: Past, present and future," *Appl. Chem. Eng.*, vol. 30, no. 3, pp. 261–279, 2019, doi: 10.14478/ace.2019.1035.
 38. M. J. Gázquez, J. P. Bolívar, R. Garcia-Tenorio, and F. Vaca, "A Review of the Production Cycle of Titanium Dioxide Pigment," *Mater. Sci. Appl.*, vol. 05, no. 07, pp. 441–458, 2014, doi: 10.4236/msa.2014.57048.
 39. E. S. Teixeira *et al.*, "Building and testing a spin coater for the deposition of thin films on DSSCS," *Mater. Res.*, vol. 23, no. 6, p. e20200214, 2020, doi: 10.1590/1980-5373-MR-2020-0214.
 40. V. Tamilselvan, D. Yuvaraj, R. Rakesh Kumar,

- and K. Narasimha Rao, "Growth of rutile TiO₂ nanorods on TiO₂ seed layer deposited by electron beam evaporation," *Appl. Surf. Sci.*, vol. 258, no. 10, pp. 4283–4287, 2012, doi: 10.1016/j.apsusc.2011.12.079.
41. M. Shakeel Ahmad, A. K. Pandey, and N. Abd Rahim, "Advancements in the development of TiO₂ photoanodes and its fabrication methods for dye sensitized solar cell (DSSC) applications. A review," *Renew. Sustain. Energy Rev.*, vol. 77, no. March, pp. 89–108, 2017, doi: 10.1016/j.rser.2017.03.129.
42. B. Gomathi Thanga Keerthana, T. Solaiyammal, S. Muniyappan, and P. Murugakoothan, "Hydrothermal synthesis and characterization of TiO₂ nanostructures prepared using different solvents," *Mater. Lett.*, vol. 220, pp. 20–23, 2018, doi: 10.1016/j.matlet.2018.02.119.
43. Z. Anajafi, M. Marandi, and N. Taghavinia, "Hydrothermal synthesis of TiO₂ nanocrystals in different basic pHs and their applications in dye sensitized solar cells," *Phys. E Low-Dimensional Syst. Nanostructures*, vol. 70, pp. 113–120, 2015, doi: 10.1016/j.physe.2015.02.023.
44. 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.
45. A. Talib *et al.*, "Performance of Dye-Sensitized Solar Cell Using Size- Controlled Synthesis of TiO₂ Nanostructure," vol. 2, pp. 106–114, 2020.
46. M. A. Sánchez-García, X. Bokhimi, A. Maldonado-Álvarez, and A. E. Jiménez-González, "Effect of Anatase Synthesis on the Performance of Dye-Sensitized Solar Cells," *Nanoscale Res. Lett.*, vol. 10, no. 1, 2015, doi: 10.1186/s11671-015-0991-3.
47. M. Ahmad *et al.*, "Effects of As, P and Sb on the output voltage generation of ZnO nanowires based nanogenerator: Mitigation of screening effect by using surface modified ZnO nanowires," *Vacuum*, vol. 202, no. May, p. 111130, 2022, doi: 10.1016/j.vacuum.2022.111130.
48. K. Santhi, M. Navaneethan, S. Harish, S. Ponnusamy, and C. Muthamizhchelvan, "Synthesis and characterization of TiO₂ nanorods by hydrothermal method with different pH conditions and their photocatalytic activity," *Appl. Surf. Sci.*, vol. 500, no. September 2019, p. 144058, 2020, doi: 10.1016/j.apsusc.2019.144058.