International Journal of Advanced Science and Research
www.allsciencejournal.com
ISSN: 2455-4227
eceived: 15-05-2023, Accepted: 30-05-2023, Published: 16-06-2023
Volume 8, Issue 1, 2023, Page No. 25-30

Mini review on synthesis and applications of hydrothermally prepared transition metal oxide nanoparticles

A D Shuaibu[1*], A Y Said[2], A S Babayo[2], S A Kwalli[3]
[1] Department of Chemistry, Faculty of Science, Aliko Dangote University of Science and Technology, Wudil, Kano State, Nigeria
[2] Department of Chemistry, Faculty of Physical Sciences, Bayero University Kano, Nigeria
[3] Department of Chemistry, Rabiu Musa Kwankwaso College of Advanced and Remedial Studies Tudunwada, Kano State, Nigeria

Abstract
Transition metal oxides (TMO) NPs are particles with constituents at the nanoscale level, which is in the 1-100 nm size range. Transition metal oxide nanoparticles are used for various purposes ranging from drug delivery in the medical field to industries for making solar cells and batteries for storing energy, cosmetics, clothes, and sensor technology. Transition metal oxide NPs have attracted serious attention recently because of their unique features, which include anti-bacterial activity, oxidation resistance, and good thermal conductivity. Transition metal oxide nanoparticles such as TiO_2, ZnO, MnO_2, and FeO are synthesized either with chemicals or using green methods, which involve the use of plant extract. Transition metal oxide nanoparticles have tremendous applications in industries, and as such, there is a need to explore more about their synthesis and applications. This study aims at presenting an overview of transition metal oxide nanoparticles (TiO_2, ZnO, and MnO_2) with serious reference to the hydrothermal method of synthesis and the different reagents, as well as the reaction conditions and mechanisms involved in the synthesis.

Keywords: nanoparticles; transition metal oxides; synthesis, hydrothermal

Introduction

Transition metal oxide-based materials are well-known due to their unique physical, optical, chemical, and interfacial properties. They exhibit extraordinary variations and controllability in their original properties in small size of the order of nanometers, which are commonly attributed to quantum confinement effects and relatively higher number of surface atoms. Due to their properties, transition metal oxides are added to make composites with different other materials to enhance their properties. Applications of transition metal oxides and their composites depend on their features, such as size, surface area, structure, stability and crystallinity. Transition metal oxides nanoparticles (TMONPs) have been used in many applications such as emulsions, tertiary oil recovery, catalysis, solar energy and drugs delivery. It is highly desirable to have tunable properties during synthesis for the commercialization of TMONPs. NPs are typically synthesized by top-down and bottom-up approaches using physical or chemical methods. The top-down methods include transforming bulk materials into smaller ones, while in the bottom-up method, the substance evolves from atoms and ions to the larger particle (Pegaz *et al.*, 2006) [31].

In the physical process, nanoparticles are synthesized by high-energy ball milling, laser ablation, electro spraying, laser pyrolysis and physical vapor deposition, which are mainly energy intensive techniques (Hasan, 2015) [12]. Chemical compounds are reduced to another form in the chemical method of nanoparticle synthesis. Examples of these approaches are sol-gel, hydrothermal, micro emulsion, and polyol synthesis. The chemical method is usually favored over its physical peer because it has many advantages, such as tunable particle size and low temperature and energy requirements, which are essential for many applications ranging from drug delivery, oil recovery, catalysis, and electronic devices.

Applications of NPs are based on their properties, such as shape and size. For instance, a study by Kulkarni and Feng (2013) [17] on the drug delivery application of polystyrene NPs of different sizes (100nm, 200nm, and 500nm) showed that, in contrast to the remaining sizes, the higher cellular uptake efficiency of these NPs was detected in the 100nm size. A similar study by Pegaz *et al.* (2006) [31] on the effect of size on extravasation and photothrombic performance of four bunches of meso (p-tetracarboxyphenyl) porphyrin loaded PLA NPs with 121nm, 194nm, 250nm, and 343nm sizes showed that, based on their compactness in size, PLA particles were favored. Furthermore, the shape of NPs can equally influence the reactivity and selectivity of a catalyst owing to difference in binding energy of adsorbates. Baquero *et al.* (2018) [4] reported that platinum NPs of similar size (about 1nm diameter) but different shape showed distinct catalytic properties. Their study has outlined the effect of shape and size of nanomaterials and why their shape must be regulated during the synthesis process. Hence, any method capable of controlling the size and shape of the nanomaterials is ideally suited for a range of applications. As mentioned in the literature, the hydrothermal method is one of the most appropriate techniques capable of regulating the size and shape of nanomaterials. This review focuses on the synthesis and applications of certain transition metal oxides nanoparticles such as TiO_2, ZnO, and MnO by hydrothermal process.

Methodology

A thorough search was conducted using the phrases "transition metal oxides," "nanoparticles," "transition metal oxide nanoparticles," and "hydrothermal synthesis of nanoparticles" across a number of electronic databases, including Google Scholar, ScienceDirect, Semantic Scholar, and PubMed. Between 2006 and 2022, studies on the synthesis and practical application of hydrothermally produced transition metal oxide nanoparticles were considered for inclusion. 50 studies in all were chosen for this study. The studies were carefully examined, and the necessary data was extracted for synthesis.

Hydrothermal synthesis

Hydrothermal synthesis is commonly known as crystal synthesis or crystal growth under high temperature and high-pressure water conditions of substances that are insoluble under normal temperature and pressure. It is one of the well-entrenched synthetic techniques for the preparation of transition metal oxides NPs as well as mixed oxide composites. The synthesis via hydrothermal method is generally conducted at a temperature of less than 100°C and a pressure of 1atm. During hydrothermal process, the particle size of metal oxide depends on the rate of hydrolysis and the solubility of metal oxide. To monitor the solvent field during nucleation and crystallization of the particles, the hydrothermal temperature and pressure conditions in sub-critical and super-critical water can be varied. The Hydrothermal synthesis of TMO NPs in supercritical water has benefits especially in the preparation of multi-metal oxide compounds. Hydrothermal process has several other advantages as many phases can be prepared at much lower temperatures than would be required for a solid-state reaction in hydrothermal process. For example, the magnetoplumbite stage, $BaFe_{12}O_{19}$, requires heating of the oxide components, $BaCO_3$ and α-Fe_2O_3 at around 1250°C, but the hydrothermal process can be performed at a much lower temperature (Chen *et al.*, 2020) [7].

1. Synthesis of TiO_2 nanoparticles using hydrothermal method

Hydrothermal method is among the simplest and most effective synthetic pathways for TiO_2 NPs preparation. Naghibi and co-workers (2014) [27], has reported the synthesis of TiO_2 NPs via hydrothermal assisted sol-gel technique, using titanium isopropoxide as a precursor. They observed that the TiO_2 NPs prepared by the hydrothermal assisted sol-gel method have a globular or cubic shape with a narrow particle size distribution of 2-12 nm. But the TiO_2 nanoparticles synthesized with the conventional sol-gel method has a wide particle size distribution of 4-36nm.

In 2012, Jae-Kyung and co-workers were able to synthesize TiO_2 nanostructures through the hydrothermal method by employing titanium isopropoxide as precursor. The anatase, rutile and mixed-phase TiO_2 crystal structures of size 5.7 nm, 5.4 nm and 4.4 nm respectively were determined utilizing hydrochloric acid concentrations. They noted that, after increasing the reaction time, the rutile crystallites were grown into one-dimensional nanomaterials (Oh *et al.*, 2009) [29]. The synthesis of TiO_2 nanostructures of 20 nm through the hydrothermal method using Ti $(SO_4)_2$ and strong ammonia water as titanium precursor and precipitant, respectively, was reported in a similar study by Xiaoming (2015) [48]. Their SEM and TEM analysis results confirmed that the size of TiO_2 nanostructures prepared without ammonia water exceeded nanometer size range. However, the addition of ammonia water led to substantial decrease in size of TiO_2 particles (Xiaoming, 2015) [48].

There are extensive studies where Al, Sn, and Ni-doped TiO_2 nanostructures are synthesized and explored for their structural, optoelectronic, luminescence, photocatalytic and thermal properties (Murashkina *et al.*, 2015) [26]. Yong *et al* reported synthesis of Ag decorated TiO_2 NPs by hydrothermal method with enhanced photovoltaic properties (Dong *et al.*, 2019) [9]. There are reports of one-pot hydrothermal synthesis of Sn-doped TiO_2 aggregates. The prepared rutile and anatase aggregates of TiO_2 nanostructures were strongly crystalline. Synthesis of carbon doped TiO_2 thin film through a combination of various methods, including hydrothermal is also reported in literature where nanorod morphology was tuned after calcination at 800°C for 2 hr. The same study revealed that the substituted carbon atoms incorporated by the replacement of oxygen atoms in the lattice structure of TiO_2 was responsible for the narrowing of the TiO_2 band-gap energy (Rasoulnezhad *et al.*, 2017) [34].

Likewise, through the hydrothermal method, Chen *et al.*, (1995) [6] have synthesized highly oriented pure anatase TiO_2 thin film. Although, in general, NPs possess a high surface-to-volume ratio, structural features such as hollow nanoparticle structure are desirable to increase this ratio (Hasan, 2015) [12]. Limited studies have shown that simple template-assisted hydrothermal method for the synthesis of TiO_2 hollow nanostructures. In one such study, resorcinol-formaldehyde resin was used as a template for controlled hydrothermal synthesis of TiO_2 hollow spheres (Tang *et al.*, 2013) [41]. A hollow of TiO_2 NPs was synthesized using carbon sphere as a composite CS-TiO_2 forming template and then selective CS removal by calcination at 500°C. As result of their hollow structure, the prepared TiO_2 NPs showed remarkable photocatalytic performance against model phenolic pollutants (Réti *et al.*, 2017) [35].

Table 1: A summary of reported synthesis of TiO_2 nanoparticles via hydrothermal method by different research groups

Precursors	Conditions of Synthesis	Properties of NPs	Ref.
Titanium (vi) butoxide & HCl	Drying: 70C, 18h Calcination: 500C, 4h	Hollow TiO_2 NPs with average size of 30nm.	(Acevedo *et al.*, 1999) [2]
TTIP, HCl & deionized water	Stirring: 20min Heating: 130C, 24h Calcination: 400°C & 600°C.	TNTs with 51.92% of anatase at 400C & 45.36% at 600C and average size of 150nm.	(Kumar *et al.*, 2018) [18]
TTIP & M.citrifolia leaves extract.	Heating: 120°C, 8h. Calcination: 400°C, 2h.	Quasi-spherical shape NPs with size 19nm	(Sundrarajan *et al.*, 2017) [40]
Ti(OBu)4,cp), ethanol & acetone	Ultrasonication: 25°C, 30min. Heating: 90°C, 8h. Calcination: 400°C & 600°C, 2h.	Homogeneous thin film of anatase, rutile & brookite NPs.	(Dong *et al.*, 2018) [8]
Titanium oxysulfate and	Stirring: 50°C, 1h. Heating: 160°C, 20min	Crystalline NPs of 20nm size	(Pathakoti *et al.*, 2019) [30]

NaOH	Drying: 60°C, 8h.	having predominant anatase phase.	
TBT, tertbutanol and acetone.	Stirring: 5min. Heating: 130°C, 24h. Drying: 100°C, 12h. Calcination: 450°C, 2h.	Pure-polycrystalline nanorods with average size of 20nm.	(Kaya *et al.*, 2019) [16]
TTIP and hydrochloric acid	Stirring: 25°C, 1h. Heating: 150-200°C, 6h. Drying: through N_2 blowing.	Single crystal nanorods of 10nm size.	(Oh *et al*., 2009) [29]
$STiCl_4$ and distilled water	Heating: 180°C, 20h Drying: 70°C,3h	Anatase & rutile NPs with size 30 nm	(Huynh *et al*., 2018) [14]
$Ti(SO_4)_2$ and KOH	Heating: 400°C Drying: 80°C, 3h	Single phase anatase NPs with average size of 13 nm	(Mironyuk *et al.*, 2020) [25]

2. Synthesis of ZnO nanoparticles by hydrothermal method

As one of the solution-based methods for synthesizing ZnO NPs, the hydrothermal process is very simple and environmentally friendly. Several research groups have prepared ZnO nanostructures via this method, due to its easiness. The synthesis of ZnO nanostructures by combined hydrothermal and sol-gel method was reported using zinc acetate and methanol as precursors. These synthesized ZnO NPs were reported to have a smaller particle size of 14 nm than those prepared by sol-gel method which had 18 nm size (Raajshree and Brindha, 2018) [33]. In 2017, Dattatraya and co-workers were also able to synthesize ZnO NPs with granular morphology using zinc acetate, cyclohexane, and t-butyl alcohol as precursors by hydrothermal method (Bharti and Bharati, 2017) [5].

Synthesis of ZnO NPs using zinc nitrate hexahydrate as a precursor has been carried out by different research. The Synthesis was performed at 120°C in an autoclave. A study Ristić *et al.*, (2005) [36] on the template-assisted synthesis of ZnO NPs at neutral pH with tetramethylammonium hydroxide as precipitating agent. After the addition of tetramethylammonium hydroxide to ethanol and zinc acetate dehydrate mixture, ZnO NPs of size 10-20 nm were precipitated at room temperature. They found that adding water to the ethanol and zinc acetate dehydrate mixture before adding TMAH resulted in the formation of ZnO snowflakes (Ristić *et al.*, 2005) [36]. Aneesh and co-workers have also reported a work on synthesis of stable ZnO NPs through hydrothermal process by varying the growth temperature as well as concentration of the precursors. It was found that the average particle size was between 7-24 nm (Madathil *et al.*, 2007) [22].

Several research groups have synthesized doped ZnO NPs in addition to pure ZnO NPs to enhance their properties for specific applications, example in pharmacy for development of different antibiotics. To enhance the antibacterial efficacy of ZnO NPs against clinically isolated bacterial species, Saxena *et al.* (2018) [38] prepared Al-doped ZnO NPs by co-precipitation method. Related work on the preparation of pure and Sn-doped ZnO nanostructures for inhibition of pathogens was reported by Tariq Jan *et al.*, (2013) [42]. The antibacterial activity of pure ZnO and Sn-doped ZnO nanostructures were investigated against bacterial strains resistant to *E. coli*, *pseudomonas*, *staphylococcus aureus*, and methicillin. Doping ZnO with Sn paved new way to address bacterial infections of *S. aureus* particularly on the skin when used in creams.

Through the hydrothermal method, Wu *et al.*, (2014) [46] prepared Fe-doped ZnO NPs using zinc acetate and ferric nitrate as precursors. The optical and magnetic properties of Fe-doped ZnO NPs have been studied, the photoluminescence spectra of as-synthesized Fe-doped ZnO particles have been shown to exhibit slight blue shift and the UV emission has been annihilated with increasing Fe_3^+ concentration. Magnetic measurements have also shown that Fe-doped ZnO samples demonstrate ferromagnetic activity at room temperature and rising dopant concentration improves saturation magnetization. Ahmad *et al.*, (2021) [3] have reported yet another synthesis of doped ZnO nanoparticles. They synthesized a series of NPs of Ca-doped ZnO with the goal of increasing the evolution of photocatalytic hydrogen through water division under visible light illumination. The 3 mole % Ca-doped ZnO particle was found to be the most successful candidate for hydrogen evolution under visible light illumination among the series of synthesized Ca-doped ZnO NPs. They attributed small particle size, improved optical absorption, high surface area, and narrow bandgap to the increased photocatalytic performance.

Table 2: A summary of reported synthesis of ZnO nanoparticles via hydrothermal method by different research groups

Precursors used	Synthesis Condition	Properties	Ref.
Zinc acetate, rinds extract of S.rarak	Stirring: 70°C, 1hr. Drying: 95°C, 8h	1µm size nano-grain having free surfaces and boundaries	(Maryanti *et al.*, 2014) [24]
Zinc acetate and diethylene glycol	Heating: 160°C, 5h Centrifugation: 5000rpm, 30min Drying: 120°C, 24h	Regular spherical shape with size of 11 nm.	(Hu and Chen, 2008) [13]
Zinc acetate and hexamethylenetetramine	Drying: 150°C Heating: 65°C, 75°C	Urchin like morphology with average diameter of 500 nm & length of 2-3µm	(Polsongkram *et al*., 2008) [32]
Zinc nitrate, ethanol and ethylenediamine	Sonication: 40min Heating: 160°C, 20h Centrifugation and washing with water and ethanol	Nano-belt like shape with rectangular cross section and length of 10-20µm & thickness of 30-60 nm.	(Xi *et al*., 2007) [47]
$(Zn(NO_3)_2.6H_2O$, methanol, ethylene glycol and hexadecyl rime thylamm onium bromide (CTAB)	Stirring: 10min Heating: 120, 5h Centrifugation & washing.	Sphere like ZnO nanostructure with diameter of 100 nm & length of 10-15 nm.	(Saleh *et al.*, 2017) [37]
Zinc nitrate, hexahydrate, hexamethylenetetramine and ethanol	Sonication: 30s Spin coating: 3000 rpm Sintering:500°C, 5min. Heating: 120°C, 2h	Hexagonal nanoroids, modified nanoroids and pointed nanoroids structures at pH of 6, 9 and 11 respectively.	(Widiyandari *et al.*, 2020) [45]
Zinc nitrate hexahydrate and hexamethylenetetramine	Stirring: for 1h Heating: 140°C, 6h Drying: 100°C, 24h	Hexagonal structure with crystallite size of 57 nm, 44 nm and 46 nm.	(Ghosh *et al.*, 2020) [11]

3. Synthesis of MnO_2 nanoparticles by hydrothermal method

MnO_2 NPs exist in various structural forms such as α, β, γ, and δ. It has a basic structural unit of [MnO_6] which is octahedral. On the basic of different MnO_6 links, MnO_2 is categorized into three classes: the chain-like tunnel structure such as α-, β-, and γ-types, the sheet or layered structure such as δ-MnO_2, and the 3D structure such as λ-type. The properties of MnO_2 are significantly affected by their phases and morphologies. Various MnO_2 NPs have been synthesized, example single crystal MnO_2 nanowires of α and β types have been synthesized by hydrothermal method employing Mn^{2+} with oxidizing reagents such as $(NH_4)_2S_2O_8$ or $KMnO_4$ (Abulizi *et al.*, 2014) [1]. Another finding by Ma *et al* (2004) [21] have reported the synthesis of MnO_2 nanobelts with narrow size via hydrothermal method.

Table 3: A summary of reported synthesis of MnO_2 nanoparticles via hydrothermal method by different research groups**.**

Precursors used	Synthesis Condition	Properties	Ref.
$MnSO_4.H_2O$ and $(NH4)_2S_2O_8$.	Stirring: at RT Heating: 120°C, 12 h Calcination: 400°C for 2 h	Hollow, urchin and smooth ball nano-rods.	(Li *et al*., 2012) [20]
$MnCl_2.4H_2O$ and NaOH	Stirring: at RT.	Porous like particles with varying pore size.	(Shaik *et al.*, 2019) [39]
$KMnO_4$ and HCl	Stirring: 20 min. Heating: 140°C for 17 h.	Birnessite flower and alpha type tubular structure.	(Li *et al*., 2017) [19]
$KMnO_4$, Na_2SO_4 and HCl.	Stirring: 20 min. Heating: 90°C for 2 h.	Amorphous plates and flakes structure.	(Yamaguchi *et al.*, 2020) [50]
C_3N_4 and $KMnO_4$	Heating: melamine at 60°C, 4 h. Heating: 180°C, 24-30 h.	Rod like and spherical structure.	(Xu *et al*., 2018) [49]
$KMnO_4$, $MnCl_2.H_2O$ and NaOH	Stirring: 50°C, 20 min. Calcination: 400-500°C, 2 h. Stirring: Vigorous Heating: 110°C, 6 h	Plate like with slit-like pores and sphere like of ink-bottle shape.	(Teli *et al*., 2020) [43]
$MnSO_4.H_2O$ and $K_2S_2O_8$	Drying: 80°C, 3 h	Caddice-clew and urchin-like particles of size 50-100 nm.	(Yamaguchi *et al*., 2020) [50]

Applications of TMO NPs

In recent years, TMO have been widely exploited in a variety of applications. This is due to their biocompatibility, exceptional stability in different environments and their ability to generate electron-hole pairs when utilized as photocatalysts (Jana *et al.*, 2017) **[15]**. Below are some of the applications of TMO NPs for different purposes. The highly explored application of TMO NPs in wastewater treatment is their use as photo catalysts. The versatility of TMO NPs which makes them suitable as sole photocatalysts or heterostructures comprising varying compounds. The efficiency of TMO NPs as catalysts in water remediation is governed by several factors including, crystallinity, surface morphology and band gap energy. A study by Narath *et al.*, (2021) **[28]** explored the application of ZnO, NiO and CuO NPs in the degradation of water pollutants methylene blue and Alizarin red. They observed that, within a period of 180 min, the efficiency of these particles was between 80-88%.

With regard to antimicrobial activity, different studies were reported on bacterial inactivation of TMO NPs. These NPs were explored for gram-positive bacteria *S. aureus* as well as gram-negative like *Pneumoniae*. Based on the findings, the studied TMO NPs (ZnO and MnO_2) yielded better antimicrobial activity against these classes of bacteria (Wang *et al.*, 2010) [44]. TMO NPs and their composites are employed in various drug delivery applications. Iman Gholamali *et al* (2020) [10] studied the relationship between encapsulation and release of ibuprofen drug using CuO NPs at various pH. They observed a better controlled delivery as well as good swelling capacity when compared with starch. Solar cell being an alternative for fossil fuels, because solar energy is one of the abundant energy sources on the earth and more importantly being green as such it has less hazard. Mahmoudabadi and Eslami (2019) [23] recorded a conversion efficiency of 7.4% for CuO NPs. TMO NPs have been reported to have good sensitivity and selectivity compared to many other NPs as a result of high surface area per volume ratio because of their mesoporous nature.

Conclusion

This review paper has outlined the synthesis of TMONPs by hydrothermal method using different conditions and reagents. The review equally shows the incredible properties of TMNOPs makes them significantly relevant in various fields such as energy, health care, environment, agriculture etc. Transition metal oxide nanoparticle have great potentials to convert poorly soluble, poorly absorbed and labile biological active substances into reliable deliverable substances. The hydrothermal method of NPs synthesis is also very effect and less costly with assurance of producing high quality NPs.

References

1. Abulizi A, Yang GH, Okitsu K, Zhu JJ. Synthesis of MnO2 nanoparticles from sonochemical reduction of MnO4− in water under different pH conditions. Ultrasonics Sonochemistry,2014:21(5):1629-1634.
2. Acevedo S, Ranaudo MA, Escobar G, Gutiérrez X. Dynamic interfacial tension measurement of heavy crude oil–alkaline systems: The role of the counterion in the aqueous phase. *Fuel*,1999:78(3):309-317.
3. Ahmad I, Akhtar MS, Ahmed E, Ahmad M, Naz MY. Lu modified ZnO/CNTs composite: A promising photocatalyst for hydrogen evolution under visible light illumination. Journal of Colloid and Interface Science,2021:584:182-192.
4. Baquero EA, Tricard S, Coppel Y, Flores JC, Chaudret B, de Jesús E. Water-soluble platinum nanoparticles stabilized by sulfonated N-heterocyclic carbenes: Influence of the synthetic approach. Dalton Transactions,2018:47(12):4093-4104.
5. Bharti DB, Bharati A. Synthesis of ZnO nanoparticles using a hydrothermal method and a study its optical activity. Luminescence,2017:32(3):317-320.

6. Chen Q, Qian Y, Chen Z, Wu W, Chen Z, Zhou G, *et al*. Hydrothermal epitaxy of highly oriented TiO2 thin films on silicon. *Applied Physics Letters*,1995:66(13):1608-1610.
7. Chen W, Du L, Wu C. Hydrothermal synthesis of MOFs. In Metal-Organic Frameworks for Biomedical Applications Elsevier, 2020, 141-157.
8. Dong P, Cheng X, Huang Z, Chen Y, Zhang Y, Nie X, et al. In-situ and phase controllable synthesis of nanocrystalline TiO2 on flexible cellulose fabrics via a simple hydrothermal method. Materials Research Bulletin,2018:97:89-95.
9. Dong YX, Wang XL, Jin EM, Jeong SM, Jin B, Lee SH. One-step hydrothermal synthesis of Ag decorated TiO2 nanoparticles for dye-sensitized solar cell application. Renewable Energy,2019:135:1207-1212.
10. Gholamali I. Facile preparation of carboxymethyl cellulose/Cu bio-nanocomposite hydrogels for controlled release of ibuprofen. Regenerative Engineering and Translational Medicine,2020:6:115-124.
11. Ghosh R, Kundu S, Majumder R, Chowdhury MP. Hydrothermal synthesis and characterization of multifunctional ZnO nanomaterials. Materials Today: Proceedings,2020:26:77-81.
12. Hasan S. A review on nanoparticles: Their synthesis and Types. Research Journal Recent Sciences,2015:4:2502.
13. Hu Y, Chen HJ. Preparation and characterization of nanocrystalline ZnO particles from a hydrothermal process. Journal of Nanoparticle Research,2008:10(3):401-407.
14. Huynh TT, Van Nguyen A, Pham HQ, Vinh NH, Bach LG, Thanh Ho VT. One-step hydrothermal synthesis of a new nanostructure $TiO_7.IrO_3.O_2$ for enhanced electrical conductivity: The effect of pH on the formation of nanostructure. Journal of Nanoscience and Nanotechnology,2018:18(10):6928-6933.
15. Jana A, Scheer E, Polarz S. Synthesis of graphene-transition metal oxide hybrid nanoparticles and their application in various fields. Beilstein Journal of Nanotechnology,2017:8(1):688-714.
16. Kaya İC, Kalem V, Akyildiz H. Hydrothermal synthesis of pseudocubic BaTiO3 nanoparticles using TiO2 nanofibers: Study on photocatalytic and dielectric properties. International Journal of Applied Ceramic Technology,2019:16(4):1557-1569.
17. Kulkarni SA, Feng SS. Effects of particle size and surface modification on cellular uptake and biodistribution of polymeric nanoparticles for drug delivery. Pharmaceutical Research,2013:30(10):2512-2522.
18. Kumar S, Vats T, Sharma SN, Kumar J. Investigation of annealing effects on TiO2 nanotubes synthesized by a hydrothermal method for hybrid solar cells. Optik,2018:171:492-500.
19. Li N, Zhu X, Zhang C, Lai L, Jiang R, Zhu J. Controllable synthesis of different micro structured MnO2 by a facile hydrothermal method for supercapacitors. Journal of Alloys and Compounds,2017:692:26-33.
20. Li Y, Wang J, Zhang Y, Banis MN, Liu J, Geng D, *et al*. Facile controlled synthesis and growth mechanisms of flower-like and tubular MnO2 nanostructures by microwave-assisted hydrothermal method. Journal of Colloid and Interface Science,2012:369(1):123-128.
21. Ma R, Bando Y, Zhang L, Sasaki T. Layered MnO2 nanobelts: hydrothermal synthesis and electrochemical measurements. Advanced Materials,2004:16(11):918-922.
22. Madathil ANP, Vanaja K, Jayaraj M. Synthesis of ZnO nanoparticles by hydrothermal method. Paper presented at the Nanophotonic materials, 2007.
23. Mahmoudabadi ZD, Eslami E. One-step synthesis of CuO/TiO2 nanocomposite by atmospheric microplasma electrochemistry-Its application as photoanode in dye-sensitized solar cell. Journal of Alloys and Compounds,2019:793:336-342.
24. Maryanti E, Damayanti D, Gustian I. Synthesis of ZnO nanoparticles by hydrothermal method in aqueous rinds extracts of Sapindus rarak DC. Materials Letters,2014:118:96-98.
25. Mironyuk I, Soltys L, Tatarchuk T, Savka KO. Methods of titanium dioxide synthesis. Physics and Chemistry of Solid State,2020:21(3):462-477.
26. Murashkina AA, Murzin PD, Rudakova AV, Ryabchuk VK, Emeline AV, Bahnemann DW. Influence of the dopant concentration on the photocatalytic activity: Al-doped TiO2. The Journal of Physical Chemistry C,2015:119(44):24695-24703.
27. Naghibi S, Sani MAF, Hosseini HRM. Application of the statistical Taguchi method to optimize TiO2 nanoparticles synthesis by the hydrothermal assisted sol–gel technique. Ceramics International,2014:40(3):4193-4201.
28. Narath S, Koroth SK, Shankar SS, George B, Mutta V, Wacławek S, *et al*. Cinnamomum tamala leaf extract stabilized zinc oxide nanoparticles: A promising photocatalyst for methylene blue degradation. *Nanomaterials*,2021:11(6):1558.
29. Oh JK, Lee JK, Kim SJ, Park KW. Synthesis of phase- and shape-controlled TiO2 nanoparticles via hydrothermal process. Journal of Industrial and Engineering Chemistry,2009:15(2):270-274.
30. Pathakoti K, Manubolu M, Hwang HM. Effect of size and crystalline phase of TiO2 nanoparticles on photocatalytic inactivation of Escherichia coli. Journal of Nanoscience and Nanotechnology,2019:19(12):8172-8179.
31. Pegaz B, Debefve E, Ballini JP, Konan Kouakou YN, van den Bergh H. Effect of nanoparticle size on the extravasation and the photothrombic activity of meso (p-tetracarboxyphenyl) porphyrin. Journal of Photochemistry and Photobiology B: Biology,2006:85(3):216-222.
32. Polsongkram D, Chamninok P, Pukird S, Chow L, Lupan O, Chai G, *et al*. Effect of synthesis conditions on the growth of ZnO nanorods via hydrothermal method. Physica B: Condensed Matter,2008:403(19-20):3713-3717.
33. Raajshree RK, Brindha D. *In Vivo* Anticancer Activity of Biosynthesized Zinc Oxide Nanoparticle using Turbinaria conoides on a Dalton's Lymphoma Ascites Mice Model. Journal of Environmental Pathology, Toxicology and Oncology, 2018, 37(2).
34. Rasoulnezhad H, Kavei G, Ahmadi K, Rahimipour MR. Combined sonochemical/CVD method for preparation of nanostructured carbon-doped TiO2 thin film. Applied Surface Science,2017:408:1-10.

35. Réti B, Kiss GI, Gyulavári T, Baán K, Magyari K, Hernádi K. Carbon sphere templates for TiO2 hollow structures: Preparation, characterization and photocatalytic activity. Catalysis Today,2017:284:160-168.
36. Ristić M, Musić S, Ivanda M, Popović S. Sol–gel synthesis and characterization of nanocrystalline ZnO powders. Journal of Alloys and Compounds,2005:397(1-2):L1-L4.
37. Saleh SM, Soliman AM, Sharaf MA, Kale V, Gadgil, B. Influence of solvent in the synthesis of nano-structured ZnO by hydrothermal method and their application in solar-still. Journal of Environmental Chemical Engineering,2017:5(1):1219-1226.
38. Saxena V, Chandra P, Pandey LM. Design and characterization of novel Al-doped ZnO nanoassembly as an effective nanoantibiotic. Applied Nanoscience,2018:8(8):1925-1941.
39. Shaik DP, Pitcheri R, Qiu Y, Hussain O. Hydrothermally synthesized porous Mn3O4 nanoparticles with enhanced electrochemical performance for supercapacitors. Ceramics International,2019:45(2):2226-2233.
40. Sundrarajan M, Bama K, Bhavani M, Jegatheeswaran S, Ambika S, Sangili A. Obtaining titanium dioxide nanoparticles with spherical shape and antimicrobial properties using M. citrifolia leaves extract by hydrothermal method. Journal of Photochemistry and Photobiology B: Biology,2017:171:117-124.
41. Tang G, Liu S, Tang H, Zhang D, Li C, Yang X. Template-assisted hydrothermal synthesis and photocatalytic activity of novel TiO2 hollow nanostructures. Ceramics International,2013:39(5):4969-4974.
42. Tariq Jan JI, Ismail M, Zakaullah M, Naqvi SH, Badshah N. Sn doping induced enhancement in the activity of ZnO nanostructures against antibiotic resistant S. aureus bacteria. International Journal of Nanomedicine,2013:8:3679.
43. Teli AM, Beknalkar SA, Pawar SA, Dubal DP, Dongale TD, Patil DS, e*t al*. Effect of concentration on the charge storage kinetics of nanostructured MnO2 thin-film supercapacitors synthesized by the hydrothermal method. Energies,2020:13(22):6124.
44. Wang Z, Lee YH, Wu B, Horst A, Kang Y, Tang YJ *et al*. Anti-microbial activities of aerosolized transition metal oxide nanoparticles. *Chemosphere*,2010:80(5):525-529.
45. Widiyandari H, Wardani A, Indriani N, Kusumandari. Synthesis and characterization of ZnO/Pt photocatalyst materials with Pt variation by hydrothermal method. In AIP Conference Proceedings, 2020.
46. Wu X, Wei Z, Zhang L, Wang X, Yang H, Jiang J. (2014). Optical and magnetic properties of Fe doped ZnO nanoparticles obtained by hydrothermal synthesis. *Journal of Nanomaterials*.
47. Xi, Y., Hu, C., Han, X., Xiong, Y., Gao, P., & Liu, G. Hydrothermal synthesis of ZnO nanobelts and gas sensitivity property. Solid State Communications,2007:141(9):506-509.
48. Xiaoming F. Synthesis and optical absorption properties of anatase TiO2 nanoparticles via a hydrothermal hydrolysis method. Rare Metal Materials and Engineering,2015:44(5):1067-1070.
49. Xu Y, Ren B, Wang R, Zhang L, Jiao T, Liu Z. Facile preparation of rod-like MnO nanomixtures via hydrothermal approach and highly efficient removal of methylene blue for wastewater Treatment. *Nanomaterials*,2018:9(1):10.
50. Yamaguchi Y, Aono R, Hayashi E, Kamata K, Hara M. Template-free synthesis of mesoporous β-MnO2 nanoparticles: structure, formation mechanism, and catalytic properties. ACS Applied Materials & Interfaces,2020:12(32):36004-36013.