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Green chemistry method with XRD analyzes and absorption of TiO_2 nanoparticles modified with use of choline chloride

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ABSTRACT: This research report related to nano-sized particles of tetragonal rutile phase TiO_2. We have successfully synthesized TiO_2 nanoparticles, by chemical method non-toxic and bio-safe, at lower than 100°C. This method is simple, economic and friendly for environmentally and suitable for large scale grains. Using of choline chloride, to decrease the size of commercial TiO_2 by chemical method. This procedure was based on the under appropriate conditions, such as concentrations choline chloride, different volume percent content of the ethanol and water and injection time.X-Ray diffraction was studied for analyze particles size from two way, Debye-Scherer's equation and Williamson-Hall method. The X-Ray diffraction studied for analyzes particles size. FWHM of XRD data explains the interrelationship of particle size and specific surface area. It is obtained to be particles size around of 40-60 nm and specific surface area is 20-25 $m^2.g^{-1}$. The resulted size of particles with TEM images was in agreement with Debye-Scherer's equation and Williamson-Hall method.

Keywords: *Choline chloride; Specific surface area; TiO_2 nanoparticles; Williamson and Hall plot*

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INTRODUCTION

TiO_2 nanoparticles with their wide range of applications have always attracted a lot of interest. It has one of the most frequently used minerals in recent years. It is well known fact that TiO_2 has three crystalline forms of anatase, rutile and brookite (Zallen & Moret, 2006). Among these three crystalline forms, rutile phase is the most thermodynamically stable, whereas brookite and anatase are metastable and transformed to rutile on heating. Different synthesis methods such as sol-gel (Garbani, *et al.,* 2009, Thangavelu, *et al.,* 2013) microemulsion or reverse micelles (Stathatos, *et al.,* 1997) and hydrothermal synthesis (Zhang & Linli, 2007) have been used to derive the nanoparticles of TiO_2. It is widely used in the coating industry, but its small nanoscale particles have been used extensively for its unique properties such as being electrical, optical and in photocatalytic applications for environmental remediation (Wang, *et al.,*2004, Xua, *et al.,* 2008, Ramakrishna & Ghosh, 2003). TiO_2

nanoparticles are usually used in suspension state forhigh catalytic surface area and activity (Modestov & Lev, 1998). It is also used to purify, disinfect, dye, destroy cancer cells, paper making, make health and beauty, prepare UV protective coatings (the most important reason for its ability to absorb ultraviolet radiation) and make luminosity. As you know, photocatalyst is a substance that results in a chemical reaction due to light exposure, but does not undergo any changes and only provides the conditions for the reaction (Armelao, 2007). Some of the particle characteristics that are effective in photocatalytic activity include particle size, crystal structure, hydroxylation surface, absolute crystallization, light irradiation, surface absorption and preparation method. Some applications for TiO_2 are also strongly dependent on the crystalline structure and morphology (Wenbing, *et al.,* 2009, Tomkiiewicz, 2000). These particles can help convert nitrogen oxides to oxygen and nitrogen, to decompose organic matter into carbon dioxide and water (Li, *et al.,* 2002). A crystalline phase is necessary when it is considered to be a particular application, such as photocatalytic or semi conductive. For example, the anatase phase is used for sensitive light and light catalytic colors, and the rutile phase is the most frequently used phase in high-temperature sensors oxygen (Xiao, *et al.,* 2009). Sometimes there are the problem of in the traditional preparations, is that the growth of TiO_2 nanocrystalline takes a long time. A new group of green solvents may be replaced by often hazardous organic solvents in many applications. The use of ionic liquids as eutectic solvents in the preparation of nanoparticles can be replaced instead of using other methods. Ionic liquids have many advantageous characteristics, including high polarity, high ionic conductivity, negligible vapor pressure, and good thermal stability for various chemical and biological industries, one of the most pressing concerns the development of “greener”, lower cost, and more efficient solvents (Shipeng & Samar, 2006). Therefore, naturally ionic liquids “greenness” is often used more than other solvents due to their self-destructive, degradability, compatibility and stability. They have been used widely in the preparation of nanostructure inorganic materials (Andrew, *et al.,* 2005). Some of these solvents are a new group of solvents. Deep eutectic solvents (DESs) could be prepared by simply mixing choline chloride (quaternary ammonium salt) and urea, which isorganic, compounds (Abbott, *et al.,* 2004, Andrew, *et al.,* 2009, Ma,*et al.,* 2010). Thus, they are important to form nanoparticles processes in which the crystalline form and size are controlled or controllable. Urea and choline chloride can be simply mixed in a 2/1 molar ratio to form a DES (denoted as CCU) such as eutectic solvent. One characteristic of the CCU is a good solvent for many metal oxides, such as CuO, NiO, and especially ZnO. The CCU solvent will be lost when the solution is mixed with water or ethanol (Shipeng & Samar, 2006, Zhang, *et al.,* 2001, Xiao Xia & Kyung, 2016). In all of these cases,

when applying CCU solvent, the particle size is reduced greatly Dong, *et al.,* 2010). In the proposed study, we have made an attempt to prepare tetragonal pure rutile phase TiO_2 nanoparticles in a simple way. The ionic liquids such as choline chloride solvents used in the synthesis steps are completely separated from the particles, so we believe that the product is biocompatible and bio-safe and can be easily used for food and medicinal industries. In this method uses commercial TiO_2 powders as the raw material, choline chloride (ionic liquids) as the solvent, and ethanol -water mixtures as the crystallized agent. The particle size of the sample estimated from Debye-Scherer formula and Williamson-Hall method around is 59-69 nm.

MATERIALS AND METHODS

Preparation of TiO_2 Containing choline chloride

Substances of lower purity are used. Choline chloride, ethanol, powders commercial TiO_2 the raw material and deionized water as the starting materials used. A typical process involved 15 g of choline chloride, mixed with 0.5 g of powders commercial TiO_2. The reaction was carried out at 90°C were kept under slow - speed constant stirring on a magnetic stirrer for 10 hours. For the growth of TiO_2, whole of TiO_2-containing choline chloride was injected into 50 ml of mixture of ethanol - water 90/10 vol % in 5minutes in a water bath maintained at 90°C, followed by vigorous stirring for 10 hours. The resultant white suspending solid was collected by centrifugation at 5000 rpm for 30 min and dried (100°C, 3hours).

Characterizations

The morphology and size of TiO_2 of the products were examined with a transmission electron microscope (TEM); model ZEISS, EM 10C-100KV. The structure and phase purity and size of particles of prepared samples were examined by using powder X-ray diffraction. The XRD with model Phillips, PW-1730, with Cu $K\alpha$ radiation, wavelength=1.54 A° and filter wide range of Bragg's angles or scan speed: $10^\circ \leq 2\theta \leq 80^\circ$. The XRD with scan speed standard 10, depending on measurement conditions.

RESULTS AND DISCUSSION

Chemical treatment of commercial TiO_2 powders could generate TiO_2 nanoparticles when the applied conditions are appropriate. The preparation of TiO_2 nanoparticles from amorphous and impurity TiO_2 was studied at chemical conditions (T=90°C, time=10 hours). The ethanol-water mix with ratio of 90/10 vol % used as acrystallization agent and washing solution sediment particles. The residence time of TiO_2 in the choline chlorideand crystallization agent causes the loss of impurities by commercial TiO_2 and formation of nannocrystalin particles. The method of preparation by low temperature usually leads to the formation of special and unique phase. Another feature of this method is the enough

growth time of TiO_2 crystals for the formation of TiO2 nanoparticles (Dong, et al., 2010). Here, the results of analyzes carried out are examined.The X-ray diffraction patterns of the synthesized TiO_2 nanoparticles are shown in Fig.1.

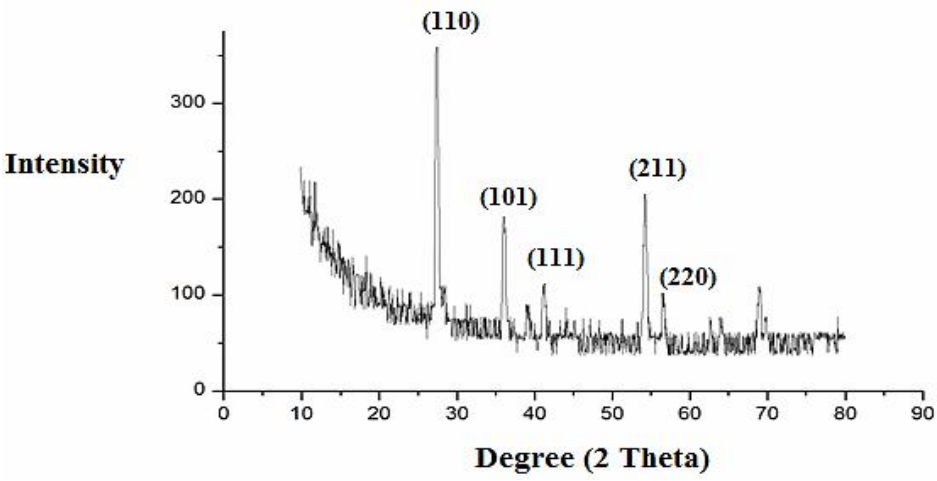

Fig.1. XRD pattern of the synthesized TiO_2 nanoparticles.

The peak details for the synthesized TiO_2 nanoparticles according to the Fig. 1 are in the Table 1. Researchers shown that absence of diffractions indicates the crystallographic purity (Varshney, *et al.,* 2010). The peaks for sample located at 27.38391°, 35.958320°, 41.2000°, 54.23322°, 56.554240° correspond to the (110), (101), (111), (211), (220) planes of the rutile phase based on the card number (JCPDS 01-077-0441 (Xu *et al.,* 2008). The intensity of peaks of the samples is directly related to the crystalline structure and show that the particle size is very small (Theivasanthi & Alagar, 2013). Better than is, orientations (110), (101), (111), (211), (220) of TiO_2 nanoparticles are selected to geometrically to be determined the crystallite size and strain in that sample (Many *et al.,* 2015). The indicate peaks can be found on the powder diagrams obtained in Fig. 1 and Table 1. No peak for the brookite and anatase structure was identified in the qualitative analysis and no impurity was found.The average crystallite size of TiO_2 nanoparticles was estimated according to the Debye-Scherer's equation (Monshi*et al.,* 2012, Aghazadeh & Aghazadeh, 2017). The emphases of the broadening of peaks proofs grain refinement along with the small strain associated with the powder. When analyzing the diffraction pattern from the sample, the instrument contribution to the peak width must be removed. The instrument contribution is convoluted with the specimen contribution to peak broadening. Peak deconvolution is difficult process, so simple calculation is often used. Most commonly, the observed peak width is treated as the sum of the squares of the

instrument and specimen contributions. The instrumental broadening (β_{hkl}) was corrected corresponding to each diffraction peak of TiO_2 material using the equation 1 (Mote *et al.,* 2012):

$$(1)\ \beta_{hkl} = \left[\left(\beta_{hkl}\right)^2_{Measured} - \left(\beta_{hkl}\right)^2_{Instrumantes} \right]^{1/2}$$

The crystallite size broadening, peak width due to crystallite size varies inversely with crystallite size. The average nanocrystalline size was calculated using Debye-Scherer's formula2 as follow:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Where D is the crystal size, λ is the wavelength of the X-ray radiation (λ=0.1540 nm) for CuKα, k is usually taken as 0.9, and β is the line width at half-maximum height, and θ is the Bragg diffraction angle. The average crystallite size of the synthesized TiO_2 nanoparticles was estimated according to the Debye-Scherer's equation for sample as shown in Table 1, Fig.1, with mixture of the ethanol-water (90/10 vol %) and time of TiO_2 – choline chloride in 10 hours, has obtained ~59 nm (Mote, et al., 2012, Prabhu, et al., 2014).

Table1. XRD data of the synthesized TiO_2 nanoparticles.

2θ	sin	cosθ	FWHM(rad)	cosθβ	Size (nm)
27.38391	0.237	0.971	0.002146	0.00208	66.63
35.95832	0.31	0.951	0.002145	0.00204	67.94
41.2	0.352	0.936	0.00343	0.00321	43.17
54.23322	0.455	0.89	0.00343	0.00305	45.44
56.55424	0.474	0.880	0.002146	0.00189	73.33
Average size (nm)	-	-	-	-	59.3

Given the Debye-Scherer's equation, it can be seen that the particle size is the smaller, the FWHM is the larger, That is, the peak is wider and its intensity is less, which is, the peak of the nanoparticles are less than that of the ordinary material and have more width. Microstructure changes affect the intensity and width of X-ray diffraction peaksis. One of the defects of the Debye-Scherer's method wasthat broadening the peaks to only dependthe size of the grains, however, studies showed that the width of the peaks was also related to the grain size and depended strains. Williamson and Hall introduced a method the grain size and intracellular strain as the X-ray diffraction broadening factor. They showed the peak width as a function of 2θ (Cullity, 1956, Ungar, *et al.,* 1984). Based on the theory introduced by Williamson-Hull, the width of the peak is at half maximum intensity, is function of particles size,

and strains inside the lattice. When Williamson-Hall plot is used, that both crystallite size and microstrain are present as equations 3, 4, 5, 6 and Fig. 2 (Many, *et al.,* 2015). Equation 3 called size broadening.

$$\beta(2\theta) = \frac{k\lambda}{L.\cos\theta} \qquad (3)$$

Equation 4 called microstrain broadening.

$$\beta(2\theta) = 4\varepsilon.\frac{\sin\theta}{\cos\theta} \qquad (4)$$

So, according Williamson-Hall plot and equation 5, 6 we can calculate both crystallite size and microstrain (Many, *et al.,* 2015).

$$\beta_{specimen} = \frac{k\lambda}{L.\cos\theta} + 4\varepsilon.\frac{\sin\theta}{\cos\theta} \qquad (5)$$

$$\beta\cos\theta = \frac{k\lambda}{Size} + 4Strain.\sin\theta \qquad (6)$$

According equation 6, when the amount of microstrain is large, the maximum observable crystallite size will be limited. The X-ray diffraction will show broadening because of particle size and strain. The smaller sizes of the particles, the peaks become the larger widths and broad. The broadening of peak will lead to occur expansion of the microstrains of the crystal structure. The observed line broadening used to calculate the average size of the particles. The total broadening of the diffraction peak is due to sample. The sample broadening was calculated using by formula 6. Williamson - Hall plot is shown in Fig.2. for the synthesized TiO_2 nanoparticles. It is plotted with sinθ on the X-axis and βcosθ on the y-axis (in radians). A linear data is got from it, so that, particle size (69 nm) and strain (3.25×10^{-5}) are extracted from y-intercept and slope respectively (Morito, *et al.,* 2003, Wu & Ma, 2006). Presence of a small amount of strain indicates a small particle size, because particles sizes of the synthesized TiO_2 nanoparticles are indirectly proportional to strain according equation 6 (Theivasanthi & Alagar, 2013). The special surface of nanoparticles is another unique property that is being investigated. The surface states are important in the nanoparticles; decrease in the particle size will increase the surface-to-volume ratio (Chen, *et al.,*2004, Ungar, 2004).

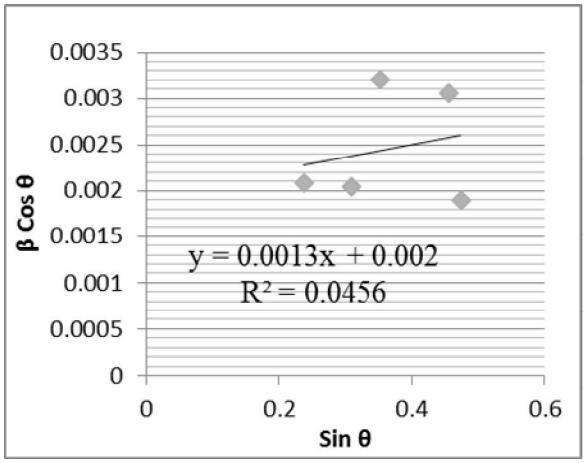

Fig. 2. Williamson-Hall plot of $B_{hkl}\cos\theta$ vs.sinθof the synthesized TiO_2nanoparticles.

By obtaining the particle size with Debye-Scherer's equation and Williamson-Hall method it is possible to calculate the specific surface area of the synthesized TiO_2 nanoparticles. Specific surface area (SSA) is a material character. It is an obtainable scientific value that can be used to determine the catalyst properties of a material. It

has aparticular importance in case of adsorption, heterogeneous catalysis and reactions on surfaces. The specific surface area and surface to volume ratio increase as the size of materials decreases (Ungar, 2004, Morito, *et al.,* 2003, Wu & Ma, 2006, Zhang, *et al.,* 2010). The SSA can be calculated using equations 7 and 8. The observed result is in Table 2 for the synthesized TiO_2 nanoparticles.

$$SSA = \frac{SA}{V_{sample} \times density_{sample}} \quad (7)$$

$$S = \frac{6 \times 10^8}{Size \times density_{sample}} \quad (8)$$

Table 2. Specific surface area of the synthesized TiO_2 nanoparticles.

Method	Particle size (nm)	Volume of cell(nm^3)	Density ($g.cm^{-3}$)	Surface Area (nm^2)	SSA ($m^2.g^{-1}$)	$SA/Volume$
Debye- Scherer's equation	59	62780	4.23	6384.41	24.04	0.101
Williamson-Hall method	69	62780	4.23	5459.13	20.56	0.087

Comparing the calculation of the size by two methods, it can be seen that, the smaller particle size, the bigger the surface to volume ratio. Other properties of TiO_2 nanoparticles are dislocation density. The dislocation density is a crystallographic defect inside of crystal structure andit is the length of dislocation lines per unit volume of the crystal (Theivasanthi & Alagar, 2013). The strong dislocation permeated many of the properties of materials. Scientist found that crystals with larger dislocation density were harder. It has been shown that the grain size decreases, the dislocation density increases, and increasing strain so, particles size of the synthesized TiO_2 nanoparticles are indirectly proportional to dislocation density (Theivasanthi & Alagar, 2013). The X-ray line profile analysis has been used to calculate the strainand dislocation density (NQ. *et al.,* 2007, Gubicza, *et al.,* 2008). The dislocation density (δ) in the synthesized TiO_2 nanoparticles has been determined using equation 9 and 10 (Ma,*et al.,* 2010). The δequal 2.84×10^{14} m^2 forthe synthesized TiO_2 nanoparticles and the results are shown in Table 3.

$$\delta = \frac{15\beta\cos\theta}{4\alpha D} \quad (9)$$

$$\delta = \frac{1}{D^2} \quad (10)$$

Where, δ dislocation density, βmeasured at half of its maximum intensity (radian) diffraction broadening, θ diffraction angle (degree), αlattice constant (nm) and D-particle size (nm).Particle

size and dislocation density are indirectly proportional (NQ, *et al.,* 2007, Gubicza,*et al.,* 2008). As the dislocation density increases, the particle size becomes smaller. As seen in the Table 3, the dislocation density value $=5.36\times10^{14}$, the particle size is 43.17nm (minimum size) andδ was 1.85×10^{14} m^2 the particle size is 73.33nm (maximum size). This is good resulted and agreement with Debye-Scherer's equation and Williamson-Hall method.So it is correlation with the particles size with rang from 43 to 73nm and specific surface area with rang from 19.34- 32.86 $m^2.g^{-1}$ and It is concluded that the smaller the particle size, the larger the special surface (Table 3) (Theivasanthi & Alagar, 2013).

Table 3. Dislocation density of the synthesized TiO_2 nanoparticles.

2θ	**FWHM (rad)**	**βcosθ**	**Size (nm)**	**Surface Area (nm^2)**	**Specific Surface Area($m^2.g^{-1}$)**	**Dislocation Density(m^2)**
27.38391	0.002146	0.00208	66.63	5653.31	21.288	2.25×10^{14}
35.95832	0.002145	0.00204	67.94	5544.30	20.88	2.16×10^{14}
41.20	0.00343	0.00321	43.17	8725.50	32.86	5.36×10^{14}
54.23322	0.00343	0.00305	45.44	8289.61	31.21	4.84×10^{14}
56.55424	0.002146	0.00189	73.33	5136.79	19.34	1.85×10^{14}

The structural characterizations were carried out using TEM. Figs.3,4 show the TEM images of the synthesized TiO_2 nanoparticles. The particles formed agglomerations, because, there are Van der Waals forces between of particles and inside of crystal lattice (Ma, *et al.,* 2011, Luo, *et al.,* 2014, Zhang, *et al.,* 2017). This is perhaps because of the small size of the particles, and the attraction between particles is enough to create the contexts to form agglomerations.In this condition identification of size of the particles is difficult.

On the images, not all the particles were measured, only the ones that were very distinct and were in the form of separate particles were measured. As seen in the TEM images of the synthesized TiO_2 nanoparticles, grain the bigger than 100 nm can be seen due to the accumulation of particles. We cannot measure these agglomerations of particles. As seen in the Fig. 3, TEM images of the synthesized TiO_2 nanoparticles consists of shaped circular particles, with an average size less than of 100nm. The condition of presses was time of the TiO_2-containing choline chloride = 8 hours and contents of ethanol-water 90/10 vol %.According Fig. 4, there was higher the reaction time between TiO_2-containing choline chloride (time of the TiO_2-containing choline chloride = 10 hours and contents of ethanol-

water 90/10 vol %), the particle size become the smaller. The Fig.4 shows with an average width of 42 nm.This is good resulted and agreement with Debye-Scherer's equation and Williamson-Hall method.

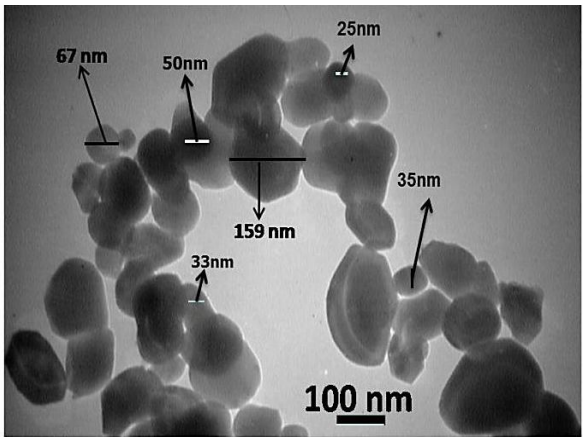

Fig. 3. TEM image of the synthesized TiO_2nanoparticles the TiO_2-containing choline chloride = 8 hours and contents of ethanol-water 90/10 vol %.

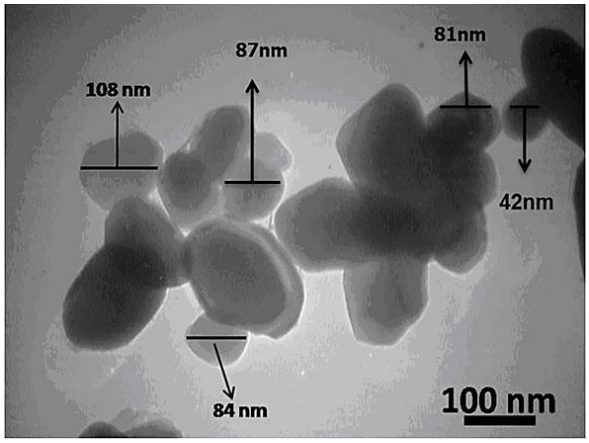

Fig. 4. TEM image of the synthesized TiO_2 nanoparticles, the TiO_2-containing choline chloride = 10 hours and contents of ethanol-water 90/10 vol %.

CONCLUSIONS

We have successfully synthesized TiO_2 nanoparticles, by chemical method non-toxic and bio-safe, at lower than 100°C. It was shown that commercial TiO_2 powders and contents choline chloride (CC) can be used as a precursor for the chemical methods of the synthesized TiO_2 nanoparticles. The nanoparticles were with shapes of circulars. This method is simple, economic and friendly for environmentally benign which will make it suitable for various applications. XRD analyses have confirmed that the synthesized particles are tetragonal rutile phase TiO_2 and their nanosize. XRD has also analyzed their various characters like size of particles, specific surface area, surface area, dislocation density with two methods. It is well expected that this synthesis technique would be extended to prepare many other important metal oxide nano structures.

REFERENCES

Abbott, A.P., Boothby, D., Capper, G., Davies, D.L., Rasheed, R.K. (2004). Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. J. Am. Chem. Soc., 126 (29): 9142- 9147.

Abbott, A.P., Capper, G., Davies, D.L., Rasheed, R.K., Shikotra, P. (2005). Selective extraction of metals from mixed oxide matrixes using choline-based Ionic liquids. J. Inorg. Chem., 44 (19): 6497-6499.

Monshi, A., Foroughi, M.R., Monshi, M.R. (2012). Modified Scherer equation to estimate more accurately nano-crystallite

size using XRD. World J. Nano Sci. Eng., 2: 154-160.

Abbott, A.P.,Collins, J.,Dalrymple, I.,Harris, R.C., Mistry, R.,Qiu, F.,Scheirer, J.and Wise,W.R. (2009).Processing of electric arc furnace dust using deep eutectic solvents. Aust. J. Chem. 62 (4): 341-347.

Cullity,B.D. (1956). Elements of X-Ray diffraction. Addison-Wesley Publishing Company.

Chen, J., Yaling, Li., Wang, Y., Yun, J., Cao, D. (2004). Preparation and characterization of zinc sulfide nanoparticles under high-gravity environment. Mat.Res.Bull., 39(2): 185-194.

Chinh, N.Q., Gubicza, J., Langdon, T.G. (2007). Characteristics of face-centered cubic metals processed by equal-channel angular pressing. J.Mater.Sci., 42(5): 1594-1605.

Stathatos, E., Lianos, P., Del Monte, F., Levy, D., Tsiourvas,D. (1997).Formation of TiO_2nanoparticles in reverse micelles and their deposition as thin films on glass substrates. Langmuir, 13 (16): 4295-4300.

Zhang, F.B. andLi,H.L. (2007).Hydrothermal synthesis of TiO_2nanofibres.Mater. Sci. Eng. C,27 (1): 80-82.

Ramakrishna, G. andGhosh,H.N. (2003).Optical and photochemical properties of sodium dodecylbenzenesulfonate(DBS)-capped TiO_2 nanoparticles dispersed in nonaqueous solvents. Langmuir, 19(3): 505-508.

Gubicza, J., Chinh, N.Q., Labra, J.L., Hegedus, Z., Szommer, P., Tichy, G., Langdon, T.G. (2008). Delayed microstructural recovery in silver processed by equal-channel angular pressing. J.Mater.Sci., 43 (16): 5672-5676.

Dong, J.Y., Hsu, Y.J., Wong,D.S.H. and Lu,S.Y. (2010).Growth of ZnO nanostructures with **c**ontrollable morphology using a facile green antisolvent method.J. Phys. Chem.C, 114: 8867-8872.

Thangavelu, K., Annamalai, R., Arulnandhi,D. (2013). Synthesis and characterization of nanosized TiO_2 powder derived from a sol-gel process in acidic conditions. Int. J. Emerging Technol. Adv. Eng.,3 (1): 636-639.

Xiaoxia,L. and Kyung,H.R.(2016). Development of deep eutectic solvents applied in extraction and separation. J. Sep. Sci., 39: 3505-3520.

Li, Y., Fan, Y., Chen, Y. (2002). A novel method for preparation of nanocrystalline rutile TiO_2 powders by liquid hydrolysis of $TiCl_4$. J. Mater. Chem., 12: 1387-1390.

Armelao, L., Barreca, D., Bottaro, G., Gasparotto, A., Maccato, C., Maragno, C., Tondello, E., Stangar, U.L., Bergant, M., Mahne,D. (2007).Photocatalytic and antibacterial activity of TiO_2 and Au/TiO_2nanosystems.Nanotechnology,18 (37): 5709.

Aghazadeh,M.,andAghazadeh,F.(2017).Effectsof deep eutectic solvents in preparation of nanoparticles TiO_2. Int. J. Bio-Inorg. Hybr.Nanomater, 6(4): 215-220.

Tomkiiewicz, M.(2000).Scaling properties in photocatalysis.Catalysis Today.58 (2-3): 115-123.

Ma, Z., Yu, J., H., Dai, S. (2010). Preparation of inorganic materials using ionic liquids. Adv. Mater. 22: 261-285.

Majeed Khan,M.A., Kumar, S., Ahamed, M., Alrokayan, S.A., Alsalhi, M.S. (2011). Structural and thermal studies of silver nanoparticles and electrical transport study of their thin films. Nanoscale.Res.Lett., 6(434): 1-8.

Modestov, A.D., Lev, O. (1998).Photo catalytic oxidation of 2,4-dichlorophenoxyacetic acid with Titaniaphotocatalyst. Comparison of supported and suspended TiO_2.J. Photochem. Photobiol. A: Chem., 112 (2-3): 261-270.

Gharbani,P., Mehrizad,A.,MotameniTabatabii,S. (2009).Synthesis of nanosized TiO_2 powder by Sol-Gel method in acidic conditions.J. IranChem.Res.,2: 145-149.

Shipeng, Q., Samar, J.K.(2006).Synthesis, processing and characterization of nanocrystalline titanium dioxide. J. Mater. Sci. Eng. A,435-436: 327-332.

Morito, S., Nishikawa, J., Maki,T. (2003). Dislocation density within lath Martensitic in Fe-C and Fe-Ni alloys. ISIJ Int., 43 (9): 1475-1477.

Ungar, T., Moghrabi, H., Ronnpagle, D., Wilkens,M. (1984). X-ray line-broadening study of the dislocation cell structure in deformed [001]-oriented copper single crystals.Acta metal.,32:333-342.

Ungar, T. (2004). Microstructural parameters from X-ray diffraction peak broadening.Scripta.Matter, 51: 777-781.

Thandavan, T.M.K.,Gani, S.M.A., Wong,C.S.,MdNor,R.(2015).Evaluation of Williamson-Hall Strain and Stress Distribution in ZnO Nanowires Prepared Using Aliphatic Alcohol.J. Nondestruct. Eval., 34(14): 1-9.

Theivasanthi, T. and Alagar, M. (2013). Titanium dioxide (TiO_2) nanoparticles - XRD analyses-an insight. Chemical physics journal,Research and Application of Material., 1(4): 36-43.

Varshney, R., Bhadauria, S., Gaur, M.S. (2010).Biogenic synthesis of silver nanocubes and nanorods using sundried Stevia rebaudiana leaves. Adv.Mat.Lett.,1(3): 232-237.

Mote, V.D.,Purushotham, Y., Dole, B.N. (2012).Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles. J.Theor. Appl. Phys., 6(6): 1-8.

Wang, W., GU, B., Liang, L., Hamilton, W.A., Wesolowski, D.J. (2004).Synthesis of rutile (α-TiO_2) nanocrystals with controlled size and shape by low-temperature hydrolysis: effects of solvent composition. J. Phys.Chem.B, 108 (39): 14789-14792.

Li, W., Gandra, N., Ellis, E.D., Courtney, Sh., Li, Sh., Butler,E.,Gao, R.(2009).pH-responsive, TiO_2-attached porphyrin for singlet oxygen

production in aqueous solution. ACS Appl. Mater. Interfaces,1(8): 1778-1784.

Xiao, X., Ouyang, K., Liu, R., Liang,J. (2009).Anatase type Titania nanotube arrays direct fabricated by ionization without annealing. Appl. Surf. Sci., 255(6): 3659-3663.

Wu, X.L., Ma, E. (2006).Dislocations in nanocrystalline grains. Appl. Phys. Lett, 88: 231-233.

Zhang, X., He, Y., M.L.,Sushko, Liu, J., Luo, L., De Yoreo, J.J., Mao, S.X., Wang, Ch., Rosso, K.M. (2017). Direction-specific van der Waals attraction between rutile TiO_2 nanocrystals. J. Sci., 356(6336): 434-437.

Xu, J., Li, L., Yan, Y., Wang, H., Wang, X., Fu, X., Li, G. (2008). Synthesis and Photoluminescence of well-dispersible anatase TiO_2 nanoparticles.J. Colloid Interface Sci., 318(1): 29-34.

Xua, J.J., Aoa, Y.H., Fua, D.G., Yuana, C.W. (2008). Low-temperature preparation of anatasetitania-coated magnetite.J. Phys. Chem. Solids, 69: 1980-1984.

Prabhu, Y.T.,Rao, K.V.,Kumar, V.S.,Kumari,B.S. (2014). X-Ray analysis by Williamson -Hall and size-strain plot methods of ZnO nanoparticles with fuel variation. WorldJ. Nano Sci. Eng., 4: 21-28.

Luo, Y.,Zhao, R., Pendry,J.B. (2014).Van der Waals interactions at the nanoscale: The effects of nonlocality. Proc. Natl. Acad. Sci. U S A,111(52): 18422-18427.

Zallen, R., Moret, M.P. (2006). The optical absorption edge of brookite TiO_2.Solid State Commun, 137: 154-157.

Zhang, H., Finnegan, M., Banfield, J.F. (2001).Preparing single-phase nanocrystallineanatase from amorphous Titania with particle sizes tailored by temperature. Nano Lett., 1: 81-85.

Zhang, J., Xiao, X., Nan, J. (2010). Hydrothermal–hydrolysis synthesis and photocatalytic properties of nano TiO_2 with an adjustable crystalline size. J.Hazardous Mat., 176: 617-622.

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