

Preparation, Stability and Photocatalytic Activity of Titania Nanofluid Using Gamma Irradiated Titania Nanoparticles by Two-Step Method

Radwa A. Elsalamony, Rania E. Morsi, Ahmed M. Alsabagh

Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt

Abstract

The aim of this research is to investigate the stability of titania nanofluid by utilizing the effect of gamma irradiation during the preparation of nano titania. Nanofluids with 0.0075-0.25 wt % loading of TiO₂ nanoparticles were prepared using a two-step method. Ultrasonic processing was applied to help the homogeneity and Sodium Dodecyl Sulfate (SDS) as anionic surfactant was added to increase the stability of the samples. UV–vis spectrometry, particle size distribution, zeta potential, Transmission Electron Microscopy (TEM) and sedimentation photo capturing were applied to visualize the stability and sedimentation rate of the prepared nanofluids. The results revealed that nanofluid prepared using TiO₂ irradiated with gamma radiation during preparation are the most stable suspension within 37 days. In addition, photocatalytic activity of nanofluids was examined using Methylene Blue dye (MB) as hazardous compound. It was found that for the same amount of TiO₂ sample used, the prepared nanofluid TiO₂ showed higher efficiency for this reaction.

Keywords: Nanofluid, γ -TiO₂, Degussa, photocatalysis and Methylene Blue dye (MB)

Introduction

Nanofluids are a new class of fluids engineered by dispersing nanometer-sized materials (nanoparticles, nanofibers, nanotubes, nanowires, nanorods, nanosheet, or droplets) in base fluids. Nanofluids can be prepared by a one-step or a two-step method. In the two-step method, the nanoparticles or nanotubes are first produced as a dry powder [1] and then dispersed into a fluid in a second processing step [2-4]. Suspension of nanoparticles in fluids provides advantages due to better dispersion behavior, less clogging and abrasion and larger total surface area. Many factors such as particle size, effect of surfactant, stability of suspension, and intrinsic thermal properties of dispersed nanoparticles, have been expected to influence the properties of nanofluids [5]. In view of the synthetic methods developed for the preparation of nanostructure TiO₂, a wide variety of approaches including flame synthesis, ultrasonic irradiation, chemical vapor deposition and sol–gel Method. Among them, Compared to other methods, sol-gel route is regarded as a good method to synthesis ultrafine metallic oxide and has been widely employed for preparing titanium dioxide (TiO₂) particles [4, 6]. TiO₂/water nanofluids with different volume concentrations from 1% to 2% were prepared by dispersing the synthesized nano particles in deionised water using ultrasonic bath and particles size was found to be ~6nm [5, 7]. Eastman et al [7], Wang et al. [8] used two-step method to produce alumina nanofluids. Murshed et al. [9] prepared TiO₂-water nano suspension by the same method. Xuan et al. [10] used commercially available Cu nanoparticles to prepare nanofluids of both water and transformer oil. Kwak et al. [11] used two-step method to prepare CuO dispersed ethylene glycol nanofluids by sonication and without stabilizers. Two-step method can also be used for synthesis of carbon nanotube based

nanofluids. Single -walled and multi-walled carbon nanotubes are first produced by pyrolysis method and then suspended in base fluids with or without the use of surfactants [12- 14].

Stability is a big issue that inherently related to this operation as the powders can easily aggregate due to strong van-der Waals force among nanoparticles. Surfactants or dispersants are generally applied to stabilize the nanofluids. Addition of surfactants lowers the surface tension of host fluids and increases the immersion of particles. Surfactants can be defined as chemical compounds added to nanoparticles in order to lower surface tension of liquids and increase immersion of particles. Several literatures talk about adding surfactant to nanoparticles to avoid fast sedimentation; however, enough surfactant should be added to particle at any particular case. In researches, several types of surfactant had been utilized for different kinds of nanofluids. Some important surfactants are: Sodium dodecyl sulfate (SDS) [15], Salt of oleic acid [16], Dodecyltrimethylammonium bromide (DTAB) [17], Hexadecyltrimethylammoniumbromide (HCTAB) [18].

Environmental pollution has recently become a severe problem worldwide [19]. Dyes are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora [20, 21]. They are also aesthetically objectionable for drinking and other purposes [22] and can cause allergy, dermatitis, skin irritation [23] and also provoke cancer [24] and mutation in humans [25].

Methylene blue (MB) (a basic and cationic dye) is the most commonly used substance for dyeing cotton, wood and silk. On inhalation it can cause difficulty in breathing, while on the direct contact it may cause permanent injury moglobinemia [26, 27]. The degradation of methylene blue was used as a test-reaction to verify the photocatalytic activity of the prepared TiO₂ nanofluid. The photodegradation was studied by monitoring the absorbance of the methylene blue solution at the absorption maximum wavelength of 664 nm. The rate of photodecomposition of methylene blue by TiO₂ can be calculated from the change in absorbance during photodegradation.

2. Experimental part

2.1. Materials

An anionic surfactant, sodium dodecyl-sulfate (referred to as SDS) in chemical grade, from Sigma Aldrich (USA), was used to stabilize the suspension. Water, the base fluid used in this study, was in the deionized form. The Methylene blue (MB) azo dye supplied by Aldrich had the following characteristics: C.I. number 52015; formula weight 319.86; λ_{\max} 665 nm.

2.2 Titanium dioxide nanoparticles

Nanoscale titanium dioxide was prepared according to a previously performed study [28]. Briefly, Ti(OH)₄ gel was obtained at room temperature by the addition of concentrated ammonia solution (35%) dropwisely to a vigorously stirred dilute solution of TiCl₄ (Fluka, 15%) until a pH 9 was attained. The ammonia solution was added dropwisely to prevent particle adhesion and sudden grain growth of particles. The white hydrous Ti(OH)₄ solution was irradiated under a ⁶⁰Co source (NCRRT) with 30 kGy and at a dose rate of 3.3476 kGy/h. The reactant solution was stirred mildly while irradiating it, so as not to become agglomerated with each other. The particles were then washed rigorously and repeatedly with bi-distilled water to remove any remaining impurities. After the solvent was evaporated at 100 °C for 24h, the precipitates were dried at 300 °C for 2 h to remove NH₄Cl, and then calcined at 500 °C for 4h. The produced titania was given the abbreviation γ -TiO₂.

2.3. Nanofluids preparation

The experiments were conducted using 0.1% SDS anionic surfactant for the stabilization of the nanoparticles dispersion, de-ionized water as a fluid and using Two-steps method [29]; After homogenization of SDS and distilled water by magnetic stirrer, nanoparticles were loaded while ultrasonication. An Ultrasonic bath (Elmasonic S15H, Germany) with frequency of 47 kHz, was used for stabilization and homogeneous dispersion of suspension for 2h. 0.1 wt % of both TiO₂ was prepared for a primary study and accordingly, a series of γ -TiO₂ was prepared in a concentration range; from 0.007 to 0.25 wt.%.

2.4. Nanofluids characterization

Characterization of the prepared nanofluids; average particles size, particles size distribution and zeta potential measured by using Dynamic light scattering (Malvern-ZS) nano-series, concentration and stability of suspension can be also monitored by UV-Visible absorption JENWAY-6505, conductivity was measured using portable conductivity meter (FE287) , transmission electron microscopy (JEOL-2100F) joined to energy dispersive X-ray spectrometer (EDX) and digital photography, was performed directly after the preparation and at different time intervals.

The crystalline structure and the different phases of titania nanoparticles were investigated via X-ray diffraction analysis (XRD) using Shimadzu XD-1 diffractometer. The phase identification was made according to the Joint Committee on Nanoparticles Diffraction Standards (JCPDS). The crystallite size, D_{XRD} was calculated according to Scherer equation [28, 30].

2.5. Nanofluids photo-catalytic activity

The photo-catalytic reaction was carried out in a cylindrical Pyrex reactor, containing 300 mL of the 25 ppm dye solution with 25 ml of TiO₂ nanofluid on a magnetic stirrer set at 300 rpm to maintain the photo-catalyst in suspension. The suspension was irradiated with UV 254 nm (8 W) pen-ray lamp. All experiments were performed at $25 \pm 1^\circ\text{C}$. In order to monitor the dye concentration in the solution, a 10 ml aliquot was analyzed using a JENWAY-6505 UV-visible spectrophotometer (at $\lambda_{\text{max}} = 664 \text{ nm}$ for MB), at the appropriate time intervals.

3. Results and Discussions

3.1. X-Ray Diffraction

The crystallinity of the prepared samples was examined by XRD analysis. XRD patterns of γ -TiO₂ and Degussa are shown in Figure 1. TiO₂ is a mixture of anatase and rutile, [JCPDS card 04-002-2751 and 00-001-1292] respectively.

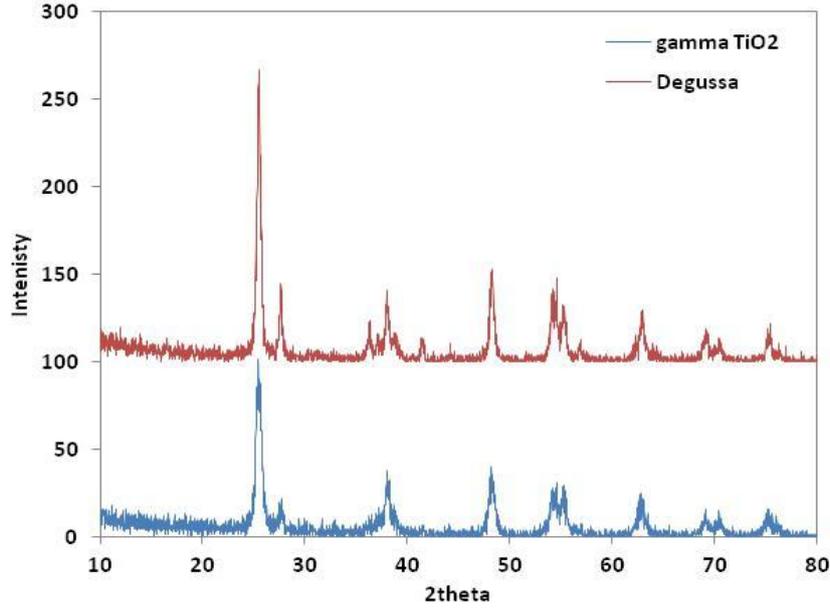


Figure 1. XRD of TiO₂ samples

The crystallite size, D_{XRD} was calculated according to Scherer equation [28, 30]. The surface area, S_{XRD} was calculated from XRD patterns using the equation

$$S_{XRD} = \frac{6}{\rho D_{XRD}} \quad [1]$$

Where; ρ is the density obtained by means of XRD [31].

The mass fraction of rutile, X_r , was determined by:

$$X_r = \frac{I_R}{0.8I_A + I_R} \quad [2]$$

Where, I_R is the intensity of predominant rutile peak (110) ($2\theta = 27.4^\circ$), and I_A is the intensity of predominant anatase peak (101) ($2\theta = 25.3^\circ$) [32]. The S_{XRD} , D_{XRD} and anatase: rutile ratios are reported in Table 1.

Table 1: Textural and structural properties of TiO₂ samples

Samples	D_{XRD} (nm)	S_{XRD} (m ² /gm)	Anatase : Rutile
γ -TiO ₂	51.5	85.5	81 : 19
Degussa TiO ₂	24.6	144	25 : 75

3.1. High Resolution Transmission Electron Microscopy (HRTEM)

The TEM images and electron diffraction (ED) patterns of TiO₂ samples are shown in Figure 2. They showed regular round shaped particles characterized to anatase phase. The larger cubic-shaped particles are crystallites of rutile. The equilibrium between the nucleation and the growth makes the formation of TiO₂ particles in the rutile possible, and the morphology of rutile is cubic-shaped. Similar findings have been encountered by Sluneco et al. [33]. In

the case of nanofluid samples; adding surfactant and applying ultrasonic, clustering and agglomeration will be less. Also; crystallinity will be decrease as comparing ED patterns.

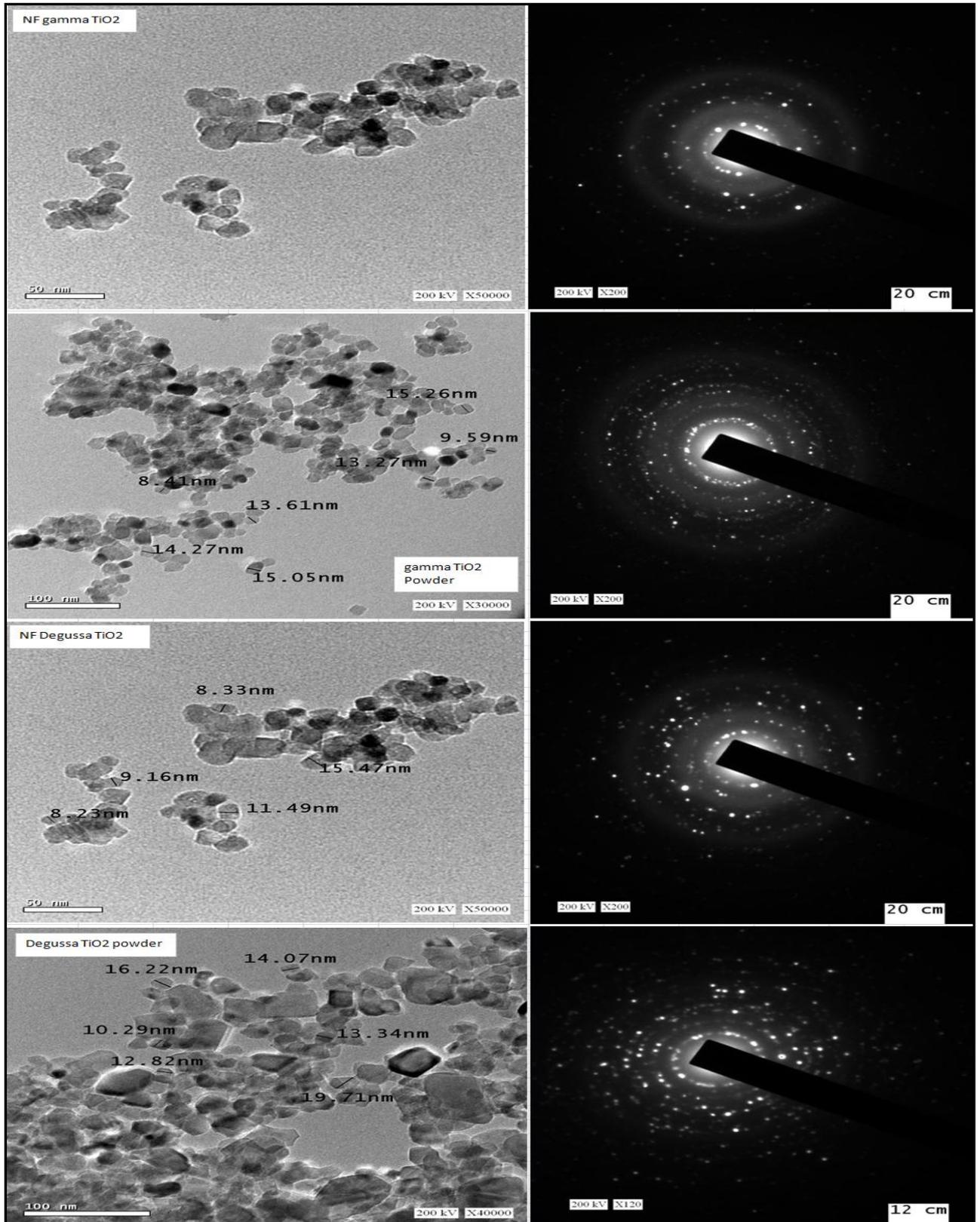


Figure 2. TEM image and ED of TiO_2 Samples

3.3. Nanofluid Stability

We prepared five concentrations (0.0075, 0.01, 0.05, 0.1 and 0.25 wt%) of titania nanofluid using γ -TiO₂ and one concentration of 0.1 wt % TiO₂ Degussa to investigate the effect of preparation method of titania nanoparticles in properties of nanofluids. Therefore, as it can be seen in Figure 3, showed fresh nanofluids, after the period of 1, 5, 15, 37 days, respectively. The nanofluids with high concentration would have a rising rate of precipitation compared to the nanofluids with low titania concentration.

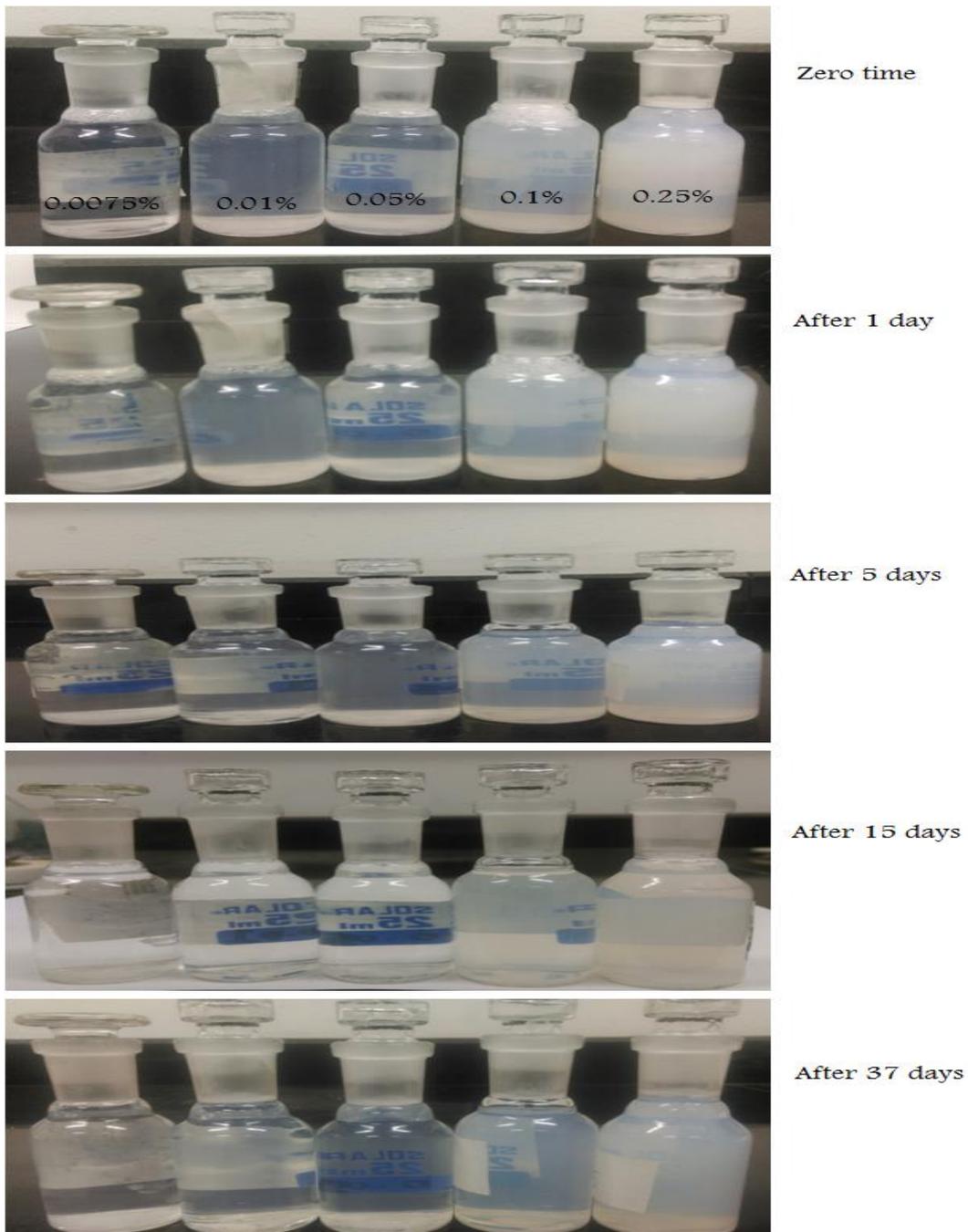


Figure 3: visual assignment of the prepared γ -TiO₂ nanofluid stability

The Sedimentation rate of nanofluid measured by UV–vis spectrophotometer [29] at wave length 320 nm. Table 2 demonstrates the concentrations of the four samples beyond 7 days. For the same amount of titania nanoparticles, the γ -TiO₂ nanofluid show most stability towards sedimentation and high conductivity than Degussa nanofluid.

Table 2. Concentrations of nanofluid TiO₂ using UV–vis spectrophotometer

Time	Concentrations (g/l)			
	γ -TiO ₂			Degussa TiO ₂
fresh	0.1	0.05	0.075	0.1
1 day	0.03383	0.03074	0.01322	0.020694
2 days	0.02811	0.02252	0.010823	0.01648
6 days	0.0281	0.0144	0	0

The effect of time on particle size can be seen in Figure 4. For three different concentration of nanofluid the particle size stay constant beyond the 7 days.

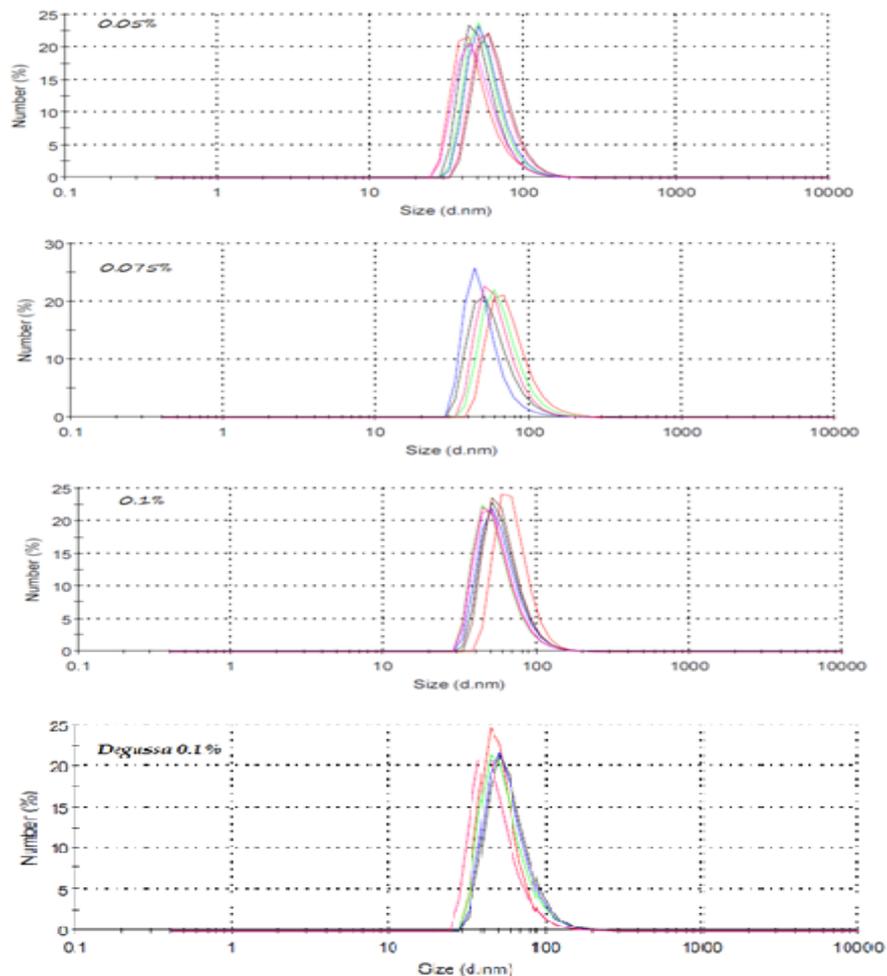


Figure 4: Particle size distribution of different concentrations of γ -TiO₂ nanofluid and 0.1 % Degussa nanofluid at time intervals; zero time, after one day, 2 days up to 7 days measured by dynamic light scatterings (DLS)

Also, we note that the γ -TiO₂ nanofluid was non-sensitive to light; whereas Degussa nanofluid color change immediately to blue as exposes to light (Figure 5). Which is a drawback usually reported during preparation of TiO₂ nanofluid [34].

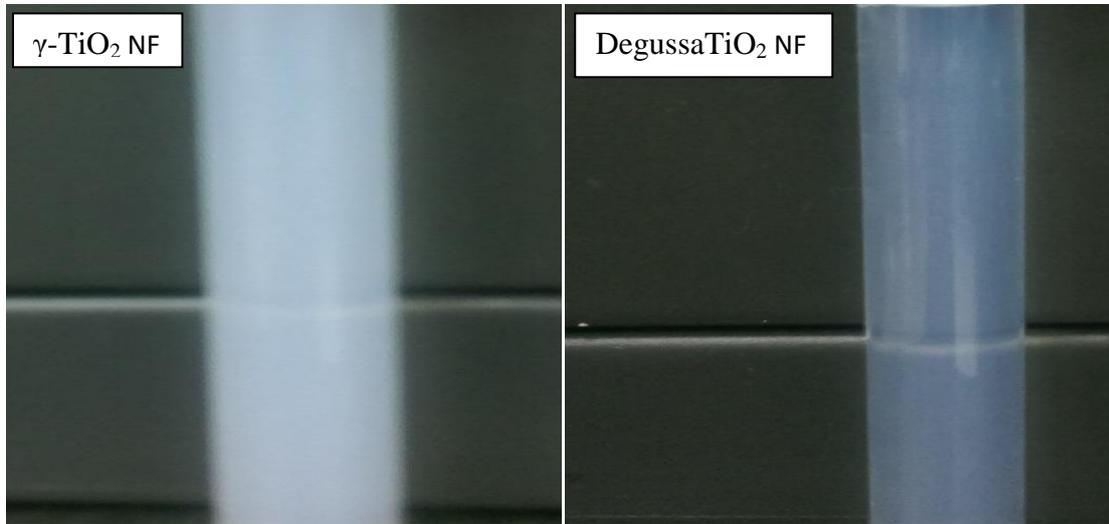


Figure 5. Effect of light on TiO₂ nanofluid

The band gaps (E_g) were calculated via UV-Vis spectroscopy using Tauc Plots, $h\nu$ can be calculated by following equation [4]:

$$E_g = h\nu = \frac{1240}{\text{wavelength of the maximum absorption}} \quad [4]$$

$$\text{For } \gamma\text{-TiO}_2 \text{ nanofluid; } E_g = \frac{1240}{294} = 4.2 \text{ e.v}$$

$$\text{For Degussa TiO}_2 \text{ nanofluid; } E_g = \frac{1240}{316} = 3.9 \text{ e.v}$$

The lower band gap energy of Degussa TiO₂ nanofluid comparison to that of γ -TiO₂ nanofluid may be cause its sensitivity to light.

Table 3 represents the average particle size, zeta potential measured by dynamic light scatterings and conductivity of nanofluids. Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the particle. The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles in dispersion. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate. Nanofluids with zeta potential from 40-60 mV are believed to have excellent stability [35]. There is a huge difference between the Zeta potential and conductivity values of the TiO₂ nanoparticles and nanofluids form. The 0.0075 nanofluid has the highest zeta potential among the prepared nanofluids.

Table 3: the average particle size, zeta potential and conductivity of titania nanoparticles and their corresponding nanofluids

	γ - irradiated TiO ₂							Non-irradiated TiO ₂ nanoparticles	
	TiO ₂ nanoparticles in water	0.0075 % NF	0.01 % NF	0.05% NF	0.075% NF	0.1% NF	0.25% NF	TiO ₂ nanoparticles in water	0.1% NF
Zeta potential	-12.5	-46.0	-40.9	-41.6	-41.4	-40.8	-37.4	-18.0	-40.8
Conductivity, mS/Cm	0.0103	0.306	0.313	0.304	0.303	0.305	0.275	0.00837	0.295
Average particle size, nm	133.3	120.2	116.4	110.7	120.2	104.3	102.0	127.1	49.05

3.4. Photocatalytic activity

The photocatalytic activity of TiO₂ nanofluid samples was tested by using methylene blue dye as a pollutant model. Before photoreaction, methylene blue was well stirred with TiO₂ nanofluid to ensure complete surface adsorption of methylene blue on TiO₂ nanoparticles. As plotted in Figure 5. A noticeable change can be observed after 60 minutes, at which point the absorbance of methylene blue had dropped greatly from 25 ppm to nearly 5 ppm, i.e. 80% of the original value. In other words, the adsorbance of dye dropped only to 15 ppm, i.e. 40% in the case of TiO₂ nanoparticles. This result indicates that the TiO₂ nanoparticles in nanofluid have strong adsorbability towards methylene blue molecules, and thus these molecules would be transferred from the solution phase to the surface of the TiO₂ nanoparticles within a short period of time, leading to the decrease in methylene blue concentration. This is because methylene blue carries a positive charge, and the pH value of TiO₂ nanoparticle suspension is (6) larger than p*H*_{zpc} (2.5) of TiO₂ nanoparticles. As a result, the surface of the TiO₂ nanoparticles carried a negative charge (Ti-O⁻), causing the TiO₂ nanoparticles and methylene blue molecules to be commonly attracted.

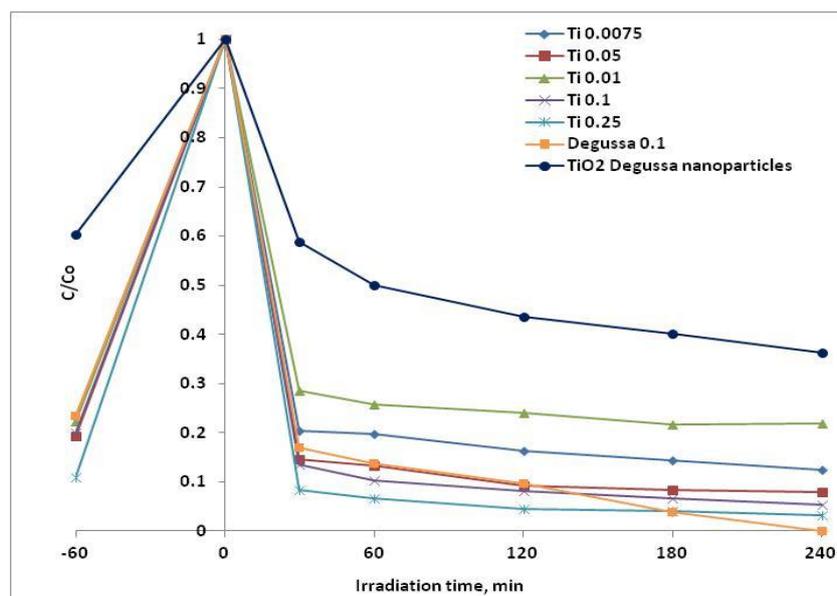


Figure 5. Photocatalytic degradation of MB under UV-irradiation using γ -TiO₂ nanofluid (0.0075, 0.01, 0.05, 0.1 and 0.25 wt%), TiO₂ Degussa 0.1% nanofluid and TiO₂ nanoparticles

Table 4. reported the rate constant of photocatalytic activity of TiO₂ nanofluid for methylene blue calculated using the apparent first order equation [36]. Upon illumination, the degradation of methylene blue reaches to maximum after 240 min in irradiation.

The result for photocatalytic decomposition of methylene blue is also compared with that of the commercial TiO₂-Degussa P25. It was found that for the same amount of TiO₂ sample used, the TiO₂ nanofluid showed catalytic properties of higher efficiency for this reaction. Since the TiO₂ nanofluid consists of highly dispersed nanoparticles, as shown in TEM images (Figure 2).

Table 4. The rate constant of photocatalytic degradation of methylene blue dye on different TiO₂ samples

Rate constant k, (min⁻¹) R²	Nanofluids					Nanoparticle	
	γ -TiO ₂ 0.0075%	γ -TiO ₂ 0.05%	γ -TiO ₂ 0.01%	γ -TiO ₂ 0.1%	γ -TiO ₂ 0.25%	Degussa 0.1%	Degussa 0.1 gm
k, (min⁻¹)	0.0026	0.0052	0.0016	0.004	0.007	0.0078	0.0032
R²	0.9732	0.9821	0.9254	0.9997	0.9969	0.9994	0.9497

This can be explained on the basis of the assumption that the photocatalytic degradation is mainly controlled by the adsorption capacity of substrate [37]. The photocatalytic activity of TiO₂ Degussa nanofluid attributed to its lowest particle size (Table 3), which increase the contact surface area between titania nanoparticles and methylene blue.

Conclusion

The present study revealed the preparation of titania nanofluid using gamma irradiated TiO₂ nanoparticles, Sodium Dodecyl Sulfate (SDS) as anionic surfactant by tow-step method. The highest stability along 37 days in high concentration nanofluid (0.25 wt %), the highest zeta potential in low concentration nanofluid (0.0075 wt %). Within the same amount of titania, TiO₂ nanofluid show highest photocatalytic degradation activity for methylene blue dye under UV irradiation comparison to TiO₂ nanoparticles. This is attributed to its lowest particle size which increases the contact surface area between nanoparticles and dye.

References

- [1] L. Cheng, F. E. P. Bandarra and J. R. Thome, *J. Nanosci. Nanotech.*, 2008; **8**, 3315-3332.
- [2] K. V. Wong and O. de Leon, *Advances in Mechanical Engineering*, 2010, **2010**, Article ID 519659, 11 pages.
- [3] Y. Nagasaka and A. Nagashima, *Journal of Physics E: Scientific Instruments*, 1981, **14** 1435– 1440.
- [4] G. Donzelli, R. Cerbino, and A. Vailati, *Physical Review Letters*, 2009, **102**, no. 10, Article ID 104503.
- [5] P. Keblinst, S. R. Phillpot, S.U.S. Choi, and J. A. Eastman, *International Journal of Heat and Mass Transfer*, 2002, **45**, 4, 855-863.
- [6] M. Arruebo, R. Fern´andez-Pacheco, M. R. Ibarra, and J. Santamar´ıa, *Nano Today*, 2007, **2**, 3, 22–32.
- [7] J. A. Eastman, U. S. Choi, S. Li, L. J. Thompson, S. Lee, *Materials Research Society Symposium-Proceedings*, Materials research Society, Pittsburgh, PA, USA, Boston, MA, USA, 1997, **457**, 3-11.
- [8] X. Wang, X. Xu, and S. U. S. Choi, *J. Thermophysics and Heat Transfer*, 1999, **13**, 474 – 480.
- [9] S. M. S. Murshed, K. C. Leong, and C. Yang, *Inter. J. Thermal Sciences*, 2005, **44**, 367– 373.
- [10] Y. Xuan and Q. Li, *Inter. J. Heat and Fluid Flow*, 2000, **21**, 1, 58 - 64.
- [11] K. Kwak, C. Kim, and Kor.-Austr. *Rheol. J.*, 2005, **17**, 35 - 40.
- [12] H. Xie, H. Lee, W. Youn, and M. Choi, *J. Appl. Phys.*, 2003, **94**, 8, 4967–4971.
- [13] P. Keblinski, J. A. Eastman, and D. G. Cahill, *Materials Today*, 2005, **8**, 6, 36-44.

- [14] M-S. Liu, M. C-C. Lin, I-T. Huang, and C.-C.Wang, *Inter. Commu. in Heat Transfer*, 2005, **2**, 9, 1202-1210.
- [15] M. Chandrasekar, S. Suresh, and A. Chandra Bose, *Exp. Therm. Fluid Sci.*, 2010, **34**, 2, 210-216.
- [16] Y. Hwang, J-K. Lee, J-K. Lee, Y-M. Jeong, S-i.Cheong, Y-C. Ahn, and S.H. Kim, *NanoparticlesTechnol*, 2008, **186**, 2, 145-153.
- [17] X.F. Li, D.S. Zhu, X.J. Wang, N. Wang, J.W. and Gao, H. Li, *Thermochim. Acta.*, 2008, **469**, 1-2, 98-103.
- [18] W. Yu, H. Xie, L. Chen, and Y. Li, *Colloids and Surfaces A.*, 2010, **355**, 1–3, 109–113.
- [19] J.Paul, K. P. Rawat, K. S. S. Sarma, and S. Sabharwal, *Appl. Radiat. Isotopes*, 2011, **69**, 982-987.
- [20] B. Royer, N. F. Cardoso, E. C. Lima, J. C. P. Vagheti, N. M. Simon, T. Calvete, and R. C. Veses, *J. Hazard. Mater.*, 2009, **164**, 1213-1222.
- [21] E. C. Lima, B. Royer, J. C. P. Vagheti, N. M. Simon, B. M. Cunha, F. A. Pavan, E. V. Benvenuti, R. Cataluna-Veses, and C. Airoidi, *J. Hazard. Mater.*, 2008, **155**, 536-550.
- [22] B. Royer, N. F. Cardoso, E. C. Lima, T. R. Macedo, and C. Airoidi, *J. Hazard. Mater.*, 2010, **181**, 366-374.
- [23] D. S. Brookstein, *Dermatol. Clin.*, 2009, **27**, 309-322.
- [24] R. O. A. Lima, A. P. Bazo, D. M. F. Salvadori, C. M. Rech, D. P. Oliveira, and G. A. Umbuzeiro, *Mutat. Res. Genet. Toxicol. Environ. Mutagen.*, 2007, **626**, 53-60.
- [25] P. A. Carneiro, G. A. Umbuzeiro, D. P. Oliveira, and M. V. B. Zanoni, *J. Hazard. Mater.*, 2010, **174**, 694-699.
- [26] V. Ponnusami, R. Madhuran, V. Krithika, and S. N. Srivastava, *Chem. Eng. J.*, 2008, 140, 609-613.
- [27] M. Rafatullah, O. Sulaiman, and R. Hashim, A. Ahmad, *J. Hazard. Mater.*, 2010, **177**, 70-80.
- [28] R. A. Elsalamony, and D. A. El-Hafiza, *Chemistry and Materials Research*, 2014, **6**, 2, 122-134.

- [29] A. Ghadimi, and I. H. Metselaar, *Experimental Thermal and Fluid Science*, 2013, **51**, 1–9
- [30] S. A. Hassan and R. A. El-Salamony, *Canadian Chemical Transactions*, 2014, **2**, 1, 57–71.
- [31] A. Maurya, P. Chauhan, S. K. Mishra and R. K. Srivastava, *J. Alloy Compd.*, 2011, **509**, 8433-8440.
- [32] R. A. Elsalamony and S. A. Mahmoud, *AJC*, 2012 article in press.
- [33] J. Slunecko, M. Kosec, J. Holc, and G. Drazic, *J. Am. Ceram. Soc.*, 1998, **81**, 1121–1124.
- [34] T. Kavitha, A. Rajendran, and A. Durairajan, *European J. Applied Engineering and Scientific Research*, 2012, **1**, 4, 235-240.
- [35] S. Mukherjee and S. Paria, *IOSR J. Mechanical and Civil Engineering*, 2013, **9**, 2, 63-69.
- [36] A. K. Aboul-Gheit, D. S. El-Desouki, and R. A. El-Salamony, *Egyptian Journal of Petroleum*, 2014, **23**, 339–348.
- [37] A. K. Aboul-Gheit , S. M. Abdel-Hamid, S. A. Mahmoud, R. A. El-Salamony, J. Valyon, M. R. Miha 1yi, and A. Szegedi, *J. Mater. Sci.*, 2011, **46**, 3319–3329.
- [38] H. Chang, C. Su, C.-H. Lo, L.-C. Chen, T.-T. Tsung and C.-S. Jwo, *Materials Transactions*, 2004, **45**, 12, 3334 – 3337.