Synthesis and characterization of TiO_2 nano fluids formation and its optical, electrical and catalytic property analysis

R. Jothiramalingam[a,*], T. Radika[b], H. A. Lohedan[a,], M. Karnan[c], D. M. Al-dhayan[a]

[a]*Department of chemistry, College of Science, King Saud University, P.O. Box. 2455, Riyadh 11451, Saudi Arabia*

[b]*Centre for Materials for Electronics Technology (C-MET), Athani, Thrissur-680581, Kerala, India*

[c]*Grassland and Forage Division, National institute of Animal Science, Rural Development Administration, South Korea*

Growing interest in the field of thermal energy conversion into useful electrical energy is the field of interest towards energy harvesting. Titania nanofluid prepared by low cost precursors using hydrothermal method. The physico chemical characterization of as prepared titania nanoparticle were characterized by XRD, Raman and UV-Visible spectrometric methods. The particle size measurement was determined *via* Zeta potential study. We have studied the miscibility and viscosity and sedimentation property of as prepared titanium dioxide nanofluid particles by low cost method in various mixed solvent medium. Nanofluids property with different concentration of TiO_2 nanoparticles (0.01%, 0.02%, 0.04%, 0.05%, 0.1%, 0.2%, 0.5%) have been prepared by adding different concentrations and studied their physico-chemical properties. The as prepared TiO_2 nanoparticles in the form fluid solution have shown very clear settled solution after the addition of suitable solvent medium and preparation method.

(Received February 13, 2023; Accepted May 11, 2023)

Keywords: TiO_2, Anatase, Catalyst, Methylene blue, Dye degradation, Nanofluids

1. Introduction

Nanofluids have recently emerged with new potential applications in heat exchangers or cooling devices being widely used in engineering applications as electronics cooling, vehicle engines, nuclear reactors, energy efficiency enhancers, food industry, air conditioning, refrigeration and biomedicine [1–6]. It has been shown that usage of nanofluids in radiators, pumps or compressors in cars the aerodynamic charge could be reduced, producing fuel savings up to 6%. A wide variety of industrial processes involve the transfer of heat energy[7,8]. The

* Corresponding author: jrajabathar@ksu.edu.sa
https://doi.org/10.15251/JOR.2023.193.283

enhancement of heating and cooling in an industrial process may create a saving in energy, reduce process time, raise thermal rating and lengthen the working life of the equipment. The development of high-performance thermal systems for heat transfer has become popular nowadays.

There are several methods to improve the heat transfer efficiency. Some methods are utilization of extended surfaces, application of vibration to the heat transfer surfaces, and usage of micro channels. Heat transfer efficiency can also be improved by increasing the thermal conductivity of the working fluid. Conventionally used heat transfer fluids such as water, ethylene glycol, and engine oil have relatively low thermal conductivities, when compared to the thermal conductivity of solids[9–11].

It was expected that heat transfer could be enhanced by dispersing micron-sized particles. But the fluid with micron- sized particles caused problems due to sedimentation and clogging. Most of all, the fluid with micron-sized particles was found to be not efficient enough. Then emerged the so called nanofluids. The mixture of nanoparticles suspended in a base fluid is usually referred to as a nanofluid. Nature is full of nanofluids, like blood, a complex biological nanofluid where different nanoparticles at molecular level accomplish different function. Addition of nanoparticles in liquid remarkably enhances energy transport process of the base fluid. Nanofluids have some unique features that are quite different from conventional two phase flow mixtures in which μm or mm particles are suspended. [12,13]

Thermal management is an application of particle dispersions wherein considerable choice exists with the material selection. Several metals, metal oxides, carbon allotropes etc. may be used for this purpose. The essential requirements of a material to be used for preparation of sub-micron dispersions for thermal management include: (i) Compare to liquid samples, high thermal conductivity of particles is required (ii) Low cost and Ease of availability of material along with nontoxicity (iii) Ease of sustenance of colloidal stability. Hence it is important to have considerations of both viscosity and thermal conductivity along with colloidal stability during the development of nanofluids. In the present work, submicron dispersions of TiO_2 in ethylene glycol-water mixture, polyethylene glycol-water mixture have been prepared by magnetic stirring of nano-sized TiO_2 particles followed by ultra-sonication. Addition of surfactant in the above Titania Nano fluids have also been studied. Hence, the appropriate experiments were conducted to prepare the pure anatase phase of TiO_2 nanoparticle in fluids for most stable, least toxic, most inexpensive and durable property.

2. Experimental

2.1 Synthesis of titania nanoparticles

Nanosized TiO_2 is prepared using hydrothermal method. The materials used are Titanium (IV) butoxide [Ti(OC4H9)4], (TBO), Sigma Aldrich], Ammonia solution. The solvents used are ethylene glycol, polyethylene glycol, double distilled water for all experiments.

2.2. Preparation of TIO_2: hydrothermal method

In this method 4 ml Titanium (IV) butoxide was taken in a beaker and about 30 ml diethanolamine was added to it with constant stirring. This solution with white colloidal precipitate was transferred into a Teflon lined autoclave and placed in an oven at 363 K for 24 h. The material obtained was centrifuged at 12,000 rpm, air dried in hot air oven (333 K) for 12 h, to obtain white crystalline powder of TiO_2. Powder was calcined at 773 K for 4 h for the formation of fine particles.

2.3. Preparation of TIO_2 based nanofluids

Two step methods were adopted for the preparation of TiO_2 nanofluids. The nanosized TiO_2 powder was weighed and dispersed into a fluid (Demineralized water, Ethylene glycol, Polyethylene glycol) in the second processing step with the help of intensive magnetic agitation and ultrasonic irradiation followed by aging treatment.

The fluid systems studied are Nanofluids with different ratio of Demineralized water, Ethylene glycol, and Polyethylene glycol (98:2,97:3,95:5,90:10,80:20,70:30,60:40,50:50) (PEG of 600, 2000, 4000). (1) Nanofluids with different concentration of TiO_2 (0.01%, 0.02%, 0.04%, 0.05%, 0.1%, 0.2%, 0.5%). (2) Nanofluids with TiO_2 prepared by different methods.(with NaOH, PEG-Urea, CTAB, Strontium titanate). Nanofluids with commercially available TiO_2.(Sigma Aldrich TiO_2). Nanofluids with varied pH (pH-2 and 4). Nanofluids added with surfactant.(CTAB).

2.4. Material characterization

The various physico-chemical methods used for the characterization of prepared TiO_2 are powder X-ray diffraction, UV-Visible spectroscopy and Raman spectroscopy. For the evaluation of the properties and stability of TiO_2 based nanofluids here employed visual observation of sedimentation of nanofluids, rheology studies of nanofluids using Rheometer and Zeta potential analysis. Powder X-ray diffraction pattern of the prepared materials were acquired using an AXS Bruker D5005 X-ray diffractometer (Germany) with a vertical goniometer. X-ray generator was operated at 40 kV and 30 ma, (Cu K α=1.54Å) radiation with Ni filter. The crystalline phase was identified by comparison with the standard JCPDS data file. Raman spectra of the sample were taken using thermo DSR Raman microscope.

2.5. Stability evaluation of nanofluids

2.5.1. Sedimentation study

Many methods have been developed to evaluate the stability of nano fluids. The simplest method is sedimentation method. The nano fluids are considered to be stable when the concentration or particle size of supernatant particles keeps constant. Ideal Nano fluids have high stability and poor suspensions, which changes the thermal and absorption properties of nanofluids drastically. Sedimentation is evaluated by gravitational sedimentation method. All Nano fluids were subjected to magnetic stirring for 2 h and ultrasonication for 1-2 h. This was kept in a measuring cylinder and observed the rate of sedimentation. Visual observation was also noted.

2.5.2. Rheology studies

Nanofluids are expected to be used under flow conditions and the flow of suspension is sometimes drastically different from that of most common heat transfer fluids that have Newtonian characteristics, it is essential to have the rheological properties of nanofluid to use in practical life. The study on the rheological properties of nanofluid may reveal the route to understand the mechanism of heat transfer enhancement and hence the design of nanoparticles for maximum heat transfer enhancement . Rheology of the TiO_2 nanoparticle dispersions of different base fluids has been investigated in terms of shear flow curve. Non-linear viscoelastic elastic measurements were done to get the flow curves for shear viscosity of nanofluids. A graph is plotted with shear rate on x-axis and viscosity on y-axis to evaluate the properties of nanofluids. Brookfield programmable DV-III + Rheometer was used to evaluate rheology of nanofluids.

2.5.3. Zeta potential analysis

Zeta potential is electric potential in the interfacial double layer at the location of the slipping plane versus a point in the bulk fluid away from the interface, and it shows the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The significance of zeta potential is that its value can be related to the stability of colloidal dispersions. So, colloids with high zeta potential (negative or positive) are electrically stabilized, while colloids with low zeta potentials tend to coagulate or flocculate. In general, a value of 25 mV (positive or negative) can be taken as the arbitrary value that separates low-charged surfaces from highly charged surfaces. The colloids with zeta potential from 40 to 60 mV are believed to be good stable, and those with more than 60 mV have excellent stability. Zeta potential analysis is an important technique to evaluate the stability. Malvern Zeta sizer is used to analyses zeta potential.

3. Results and discussion

3.1. Powder X-ray diffraction

Power XRD pattern obtained for TiO_2 prepared by hydrothermal method after calcination at 773 K for 3 h is shown in Fig 3.1. Power XRD pattern obtained for TiO_2 prepared by hydrothermal method after calcination at 773 K for 3 h is shown in Fig. 1.

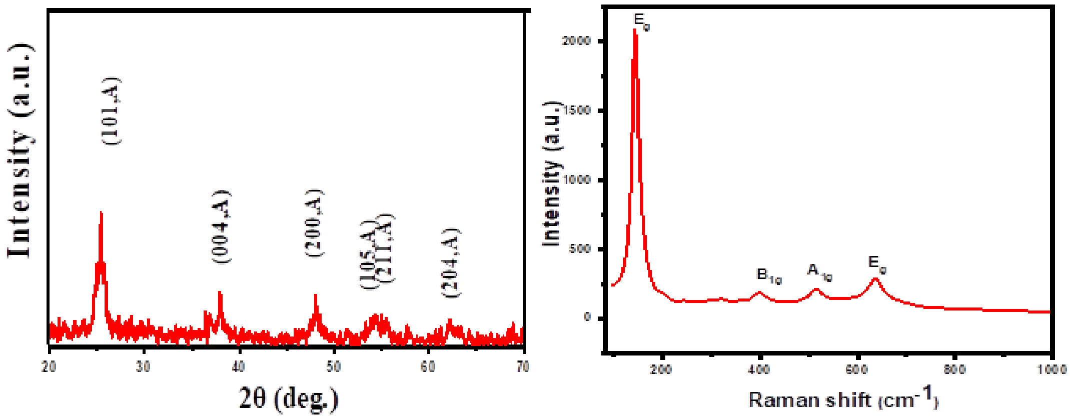


Fig. 1. (a) Powder XRD pattern of TiO_2 Nanoparticles with major anatase phase (b) Raman spectrum of hydrothermal method prepared nanoparticle of TiO_2.

The XRD pattern possess well resolved features of anatase phase with planes (101), (004), (200), (105), (211) and (204). Absence of any other peak suggests that the TiO_2 prepared through hydrothermal method consists of purely crystalline anatase phase. Figure 2 shows the UV-Visible spectra withabsorbance in the region of 250-400 nm. This absorption is corresponding to the presence of TiO_2 in the nanofluid form. Thus, it confirms the presence of uniformly distributed TiO_2 particles in the nanofluid. In the DR UV-Vis spectrum a broad strong absorption peak seen at 310 nm which is due to the reduced bandgap value of 3.0 eV by band gap calculation. This peak occurred as a result of Charge – Transfer from the valence band which basically comprises of 2p orbitals of O^{2-} ions to the conduction band which is basically made of 3d t_{2g} orbitals of Ti^{4+} cations [14,15]. To find out the bandgap value of as prepared titania nanoparticles, tauc plot was utilized in the present study.

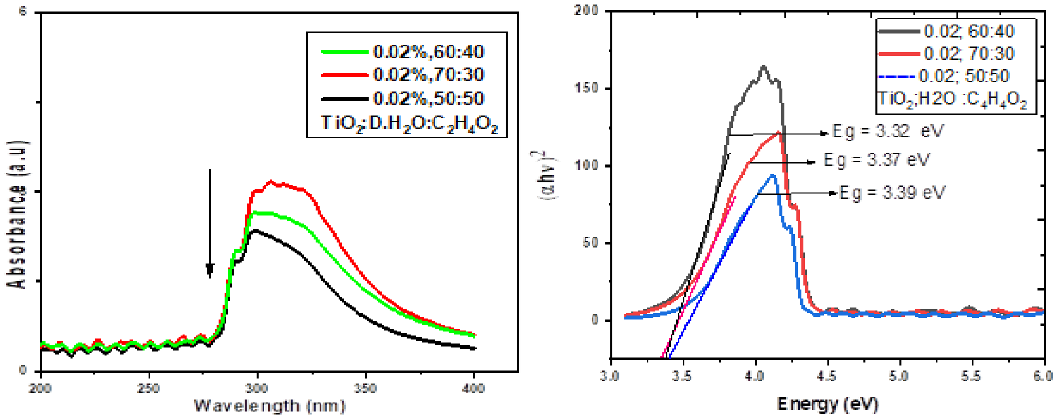


Fig. 2. (a) UV-Vis absorption spectra of titania nanoparticle at various dispersing medium (b) Band gap values of titania nanoparticle at various solvent condition.

3.3. Sedimentation study

Nanofluid with 0.02% TiO_2 concentration was found to be stable for more than four weeks (Fig.3). The selected ratio of demineralized water and ethylene glycol was 50:50 which is observed to be good in stability. Highly stable and homogeneous TiO_2 nanofluids were obtained with selected concentration of TiO_2 and solvent system.

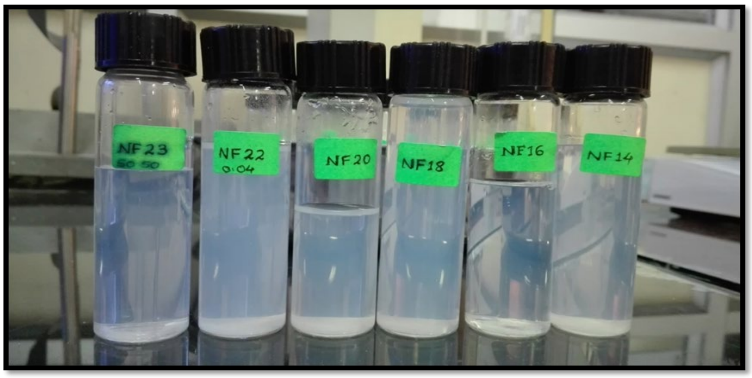


Fig. 3. Nanofluids with 0.02% TiO_2 and different ratio of dH_2O and EG/PEG.

Table 1. Nanofluids with 0.02% TiO_2 and different ratio of dH_2O and EG/PEG.

H_2O :EG/PEG	**Observation**
98:2	Light white color after 9 weeks,almost settled
97:3	Light white color after 9 weeks,almost settled
95;5	Completely settled within 2 days
90:10	Completely settled after 1 week
80:20	Completely settled in 1 week
70:30	Light white color after 6 weeks, half settled
60:40	Light white color after 5 weeks, almost settled
50:50	Light white color after 5 weeks, almost settled

Table 1 shows the effect of mixed solvent such as ethylene glycol and poly ethylene glycol addition in as prepared titania nanoparticle dispersed fluid solution. Increasing the addition of PEG, increasing the settling time of nanoparticle of Titania up to certain optimized volume of PEG addition into EG. Equal percentage addition of PEG and EG in distilled water with titania nanoparticle results in increasing the viscosity and taking more time to settle down the nanoparticle and formation of light white color clear solution.

Table 2 shows the effect of titania nanoparticle concentration addition with respect to different grades of poly ethylene glycol. From 0.1% to 0.02% of nanoparticle addition gives good results. (Figure 3). In the case of ethylene glycol and water mixture results in increasing the rate of settling down the particles (Table 3).

Table 2. Nanofluids with Poly ethylene glycol.

PEG	**Conc. TiO2 (wt.%)**	**d.H_2O:PEG**	**Observation**
PEG 200	0.1%	98:2	Completely settled within 1 day
PEG 600	0.02%	98:2	Completely settled within 1 day
PEG 4000	0.02%	90:10	Completely settled within 1 day

Table 3. Nanofluid TiO_2 and d.H_2O or EG.

Conc. Of TiO2	**System**	**Observation**
0.02%	d.H_2O+ CTAB	Almost settled ,very light white in color after 5 weeks
0.02%	d.H2O	Completely settled within 1 week
0.02%	EG	Completely settled within 1 week

Table 4 and Fig. 4 shows the effect of pH condition on formation of clear light white Nano fluid formation. In both low pH and alkaline condition favors the formation of light white color of Nano fluid with as prepared Titania nanoparticles.

Table 4. Nanofluids with the effect of different pH.

Conc. of TiO_2 nanoparticle solution	**d.H2O:EG**	**pH**	**Observation**
0.02%	98:2	2	Very light white in color, almost settled after 5 weeks
0.02%	98:2	12	Very light white in color, almost settled after 5 weeks
0.02%	50:50	2	Very light white in color, almost settled after 5 weeks
0.02%	50:50	12	Very light white in color, almost settled after 5 weeks

Finally, we have compared the time consumption rate for the formation of completely settled titania based Nano fluid with commercially available Titania (P25 Degussa) sample. The as prepared Titania nanoparticle shows faster Nano fluid formation after the addition of poly ethylene glycol (Fig. 4).

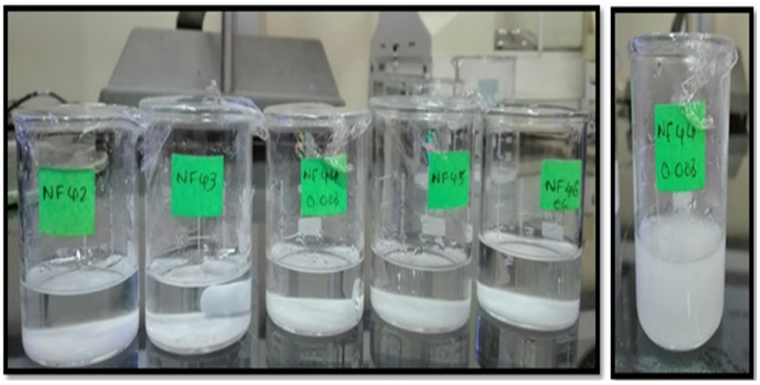


Fig. 4. (a) The comparative nanofluid formation with the addition of PEG and last image shows unclear nanofluid formation without the addition of PEG in commercial TiO_2 nanoparticle.

Table 5. Nanofluids with commercial TiO_2 (sigma Aldrich).

Concentration of TiO_2 (wt.%)	**Observation**
0.01	Completely settled within 2 days
0.02	Completely settled within 2 days
0.04	Completely settled within 2 days
0.05	Completely settled within 2 days

3.4. Rheology studies

Rheological behavior of various TiO_2 nanofluids was studied using a Rheometer. Graphical representation of viscosity versus shear rate for various nanofluid systems are shown in the following figures. The rheology behavior for 0.02 wt % TiO_2 nanofluid with various ratio of dH_2O:EG are shown in Fig 5 (a-b).

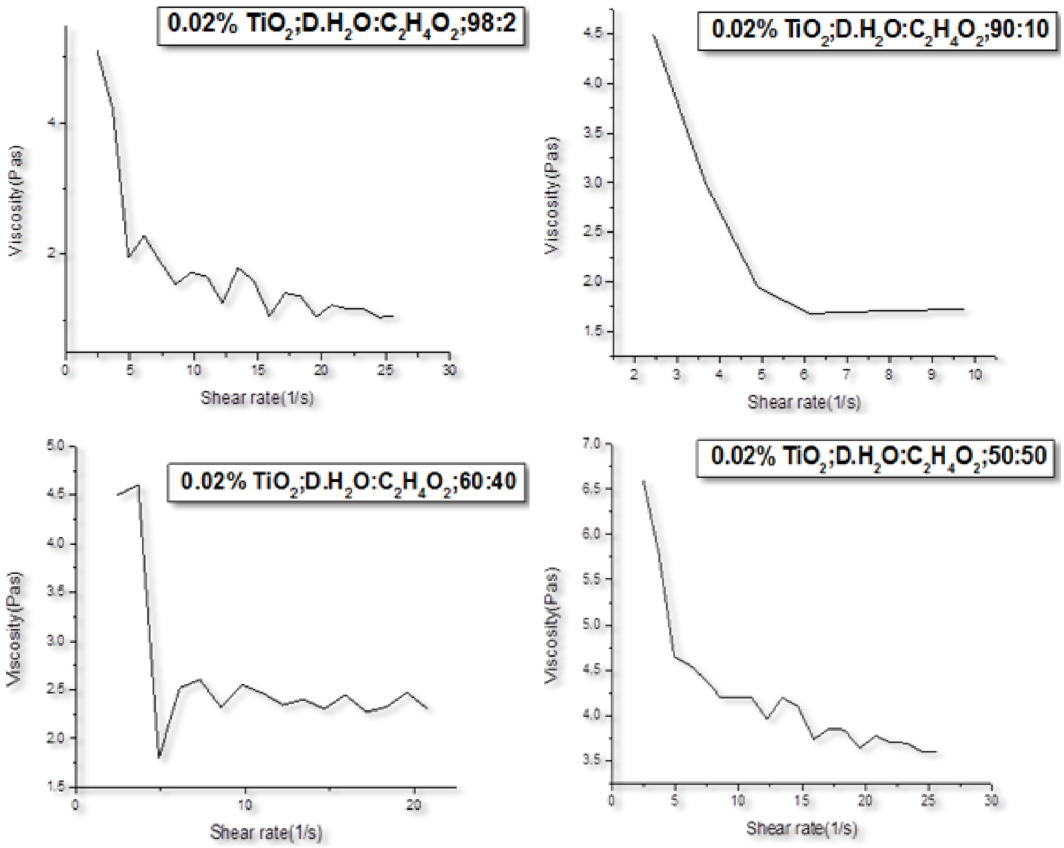


Fig. 5. (a-d) Rheology behavior for 0.02 wt % TiO2 nanofluid with various ratio of dH2O:EG.

The shear viscosity curve reveals that all dispersions are non-Newtonian with a shear-thinning viscosity. In a non-Newtonian fluid, the relation between shear viscosity and the shear rate is non-linear. Use of Ethylene glycol mixed with dH_2O (ratio 50:50) as the base fluid instead of only dH_2O seems to amplify the impact of the particle addition on the rheology of the dispersion and eventually leads to non-Newtonian behavior at lower particle loadings (0.02% TiO_2) [16]. Therefore, range of shear stress, stability and aggregation of particles should also be considered among the important factors affecting the rheology of the dispersion.

Due to the typical particle sizes involved, van der Waals forces between the particles give rise to the formation of aggregates. It is the shear induced breakup of these aggregates that give rise to the shear thinning behavior of the dispersions. No appreciable changes in the shear viscosity versus shear rate behavior were detected over the course of two weeks of dispersion for the studied systems.

3.5. Zeta potential analysis

There is a good correlation between the stability and the zeta potential have obtained. The higher the value of the zeta potential is, the greater the stability of the solution. The zeta potential analysis of the prepared TiO_2 nanofluids was carried out and the results are presented in Fig 6 (a-b)

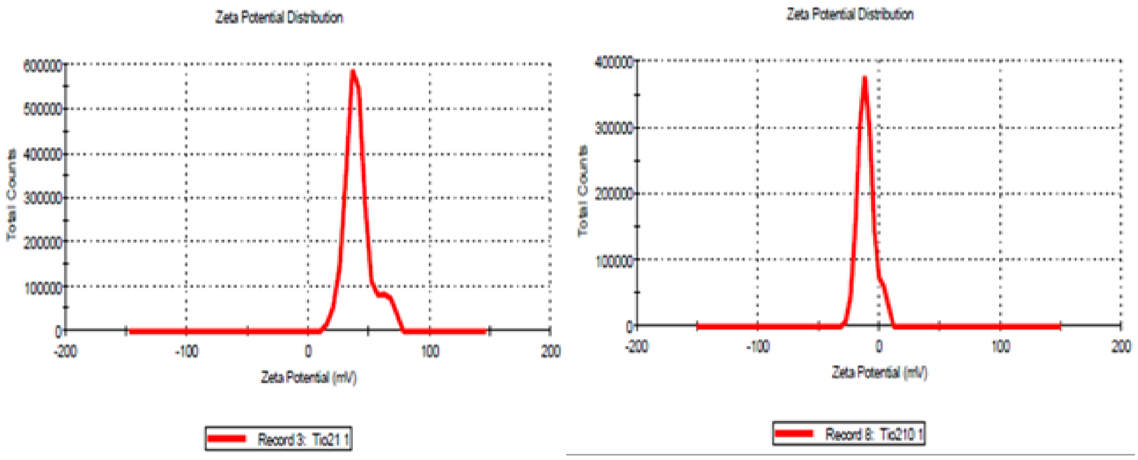
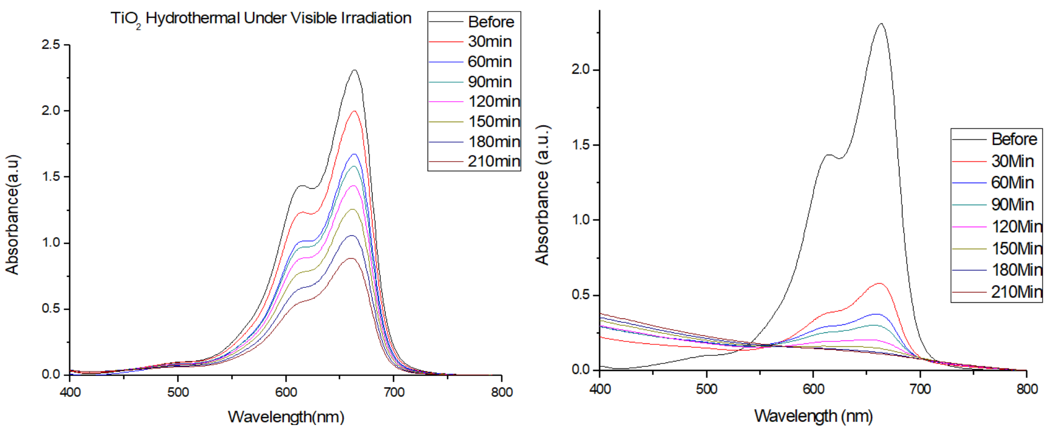


Fig. 6. Zeta potential measurement of titania nanoparticle before and after dispersed with dH2O: PEG system.

The zeta potential of TiO_2 nanofluid obtained was +40.8mV and this high value indicate the good stability obtained for the prepared Titania nanofluid after the dispersion process. Hence, the optimized addition of PEG with synthesized titania nanoparticle shows the effective nanofuid formation for thermal energy conversion application. The catalytic activity of as prepared TiO_2 nanoparticle is filtered from fluid solution and tested for visible light photocatalytic activity and the Fig 7 shows the effective degradation activity for our route prepared nanoparticle under visible light conditions [17,18].



(a) (b)

Fig. 7. Catalytic property of TiO2 nanoparticle recovered from (a) water solvent (b) EG solvent.

4. Conclusion

The XRD pattern of TiO_2 confirms the characteristic peaks for anatase TiO_2 nanoparticle formation and the reported JCPDS data matched very well with synthesized materials. The crystallite size of the TiO_2 material is in the range of 20-30 nm. Raman spectrum confirms the formation of anatase TiO_2 prepared through hydrothermal method. Effects of conditions such as concentration of nanomaterial, preparation method and concentration of surfactant have studied etc. to attain a best stable TiO_2 nanofluid system. The higher Zeta potential values have obtained for titania nanofluid system. Thermal characteristics of the nanofluid system have to be studied to make use of practical application of as prepared nanofluids as coolants for catalytic, electronics and automobiles application.

Acknowledgments

The authors (Hamad Al-lohedan) express thankful and financial support by the Researchers Supporting Project number (RSP2023R54) King Saud University, Riyadh, Saudi Arabia.

References

[1] J.R. Rajabathar, P. Arunachalam, H.A. AL-Lohedan, R. Thankappan, J.N. Appaturi, T. Pulingam, W. Mohammed Dahan, J. Sol-Gel Sci. Technol. 97 (2021) 638-650; https://doi.org/10.1007/s10971-021-05468-3

[2] J.N. Appaturi, R.J. Ramalingam, M.K. Gnanamani, G. Periyasami, P. Arunachalam, R. Adnan, F. Adam, M.D. Wasmiah, H.A. Al-Lohedan, Catalysts. 11 (2021) 1-15; https://doi.org/10.3390/catal11010004

[3] J.R. Rajabather, M.D. Albaqami, H.A. Lohedan, P. Arunachalam, K. Thirunavukkarasu, J.N. Appaturi, Surf. Interface Anal. 53 (2021) 395-405; https://doi.org/10.1002/sia.6926

[4] J.N. Appaturi, R. Jothi Ramalingam, M. Selvaraj, S. Chia, S.H. Tan, F. Khoerunnisa, T.C. Ling, E.P. Ng, Appl. Surf. Sci. 545 (2021) 149017; https://doi.org/10.1016/j.apsusc.2021.149017

[5] T. Radhika, R.J. Ramalingam, P.T. Hasna, A.M. Tawfeek, S.R.M. Syed, H. Al-Lohedan, D.M. Al-Dhayan, J. Ovonic Res. 15 (2019) 315-323.

[6] R.J. Ramalingam, J. Vijaya, H.A. Al-Lohedan, M.A. Munusamy J. Ovonic Res. 13 (2017) 13-23.

[7] J.R. Rajabathar, P. Arunachalam, Z.A. Issa, T. Ahmed M, Optik (Stuttg). 224 (2020) 165538;

https://doi.org/10.1016/j.ijleo.2020.165538

[8] R.J. Ramalingam, H. Al-Lohedan, A.M. Tawfik, G. Periyasamy, M.R. Muthumareeswaran, Chalcogenide Lett. 17 (2020) 423-428; https://doi.org/10.15251/CL.2020.178.423

[9] K. Yapici, N.K. Cakmak, N. Ilhan, Y. Uludag, Korea Aust. Rheol. J. 26 (2014) 355-363; https://doi.org/10.1007/s13367-014-0041-1

[10] J. Zhang, Y. Diao, Y. Zhao, Y. Zhang, Int. J. Heat Mass Transf. 79 (2014) 628-638; https://doi.org/10.1016/j.ijheatmasstransfer.2014.08.071

[11] D. Zhu, L. Cai, Z. Sun, A. Zhang, P. Héroux, H. Kim, W. Yu, Y. Liu, Sci. Total Environ. 787 (2021); https://doi.org/10.1016/j.scitotenv.2021.147536

[12] M. Nawaz, Phys. A Stat. Mech. Its Appl. 537 (2020); https://doi.org/10.1016/j.physa.2019.122447

[13] M. Hemmat Esfe, M. Afrand, S.H. Rostamian, D. Toghraie, Exp. Therm. Fluid Sci. 80 (2017) 384-390; https://doi.org/10.1016/j.expthermflusci.2016.07.011

[14] I. Morad, A.M. Alshehri, A.F. Mansour, M.H. Wasfy, M.M. El-Desoky, Phys. B Condens. Matter. 597 (2020); https://doi.org/10.1016/j.physb.2020.412415

[15] Y. Lin, Z. Jiang, C. Zhu, R. Zhang, X. Hu, X. Zhang, H. Zhu, S.H. Lin, Int. J. Hydrogen Energy. 42 (2017) 4966-4976; https://doi.org/10.1016/j.ijhydene.2016.06.077

[16] W. Kangwansupamonkon, N. Klaikaew, S. Kiatkamjornwong, Eur. Polym. J. 107 (2018) 118-131; https://doi.org/10.1016/j.eurpolymj.2018.08.004

[17] R. Jothiramalingama, T. Radhika,b* P. R. Aswinia , H. Al-Lohedana , M. Chandrasekaranc , D. M. Al-Dhayana , J. N. Appaturi, Digest Journal of Nanomaterials and Biostructures, Vol. 17, No. 2, April - June 2022, p. 491 – 497, https://doi.org/10.15251/DJNB.2022.172.491

[18] M. Al-Zahrani , N.S. Alsaiari, T. Radika , K. M. Abualnaja , R. Jothiramalingam , M. Ouladsmane, J. Ovonic Res. 18 (2022) 101-112, https://doi.org/10.15251/JOR.2022.181.101