Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 75 (2015) 2049 – 2054

Energy Procedia

The 7th International Conference on Applied Energy – ICAE2015

Dispersion Stability of TiO_2-H_2O Nanofluids Containing Mixed Nanotubes and Nanosheets

Xuefeng Shao[a], Ying Chen[a,]*, Songping Mo[a], Zhengdong Cheng[a,b], Tao Yin[a]

[a] *Guangdong Provincial Key Laboratory on Functional Soft Condensed Matter, School of Materials and Energy, Guangdong University of Technology, No. 100 Waihuan Xi Road,Panyu District, Guangzhou 510006, China.*
[b] *Artie McFerrin Department of Chemical Engineering, Texas A &M University, College Station, Texas 77843-3122, USA.*

Abstract

Titanium dioxide nanotubes (TiNTs) and nanosheets (TiNSs) were synthesized according to the hydrothermal synthesis method. TiO_2-H_2O binary nanofluids were prepared by dispersing certain amount of both TiNTs and TiNSs in deionized water. Stabilities of nanofluids of different total concentrations were observed visually 1 hour later after preparation to classify stable and unstable nanofluids among nanofluids containing different ratios of TiNTs and TiNSs. Sedimentation heights variations with time were measured to indicate sedimentation velocities of nanoparticles of nanofluids of different concentrations as well. The preliminary results revealed that binary nanofluids stabilities could be improved effectively when concentration ratios of TiNTs to TiNSs are at suitable range compared with TiNTs or TiNSs alone, otherwise stabilities were deteriorated seriously. We consider the phenomenon is possibly concerned with electrostatic repulsion and depletion interactions in binary nanofluids.

Peer-review under responsibility of Applied Energy Innovation Institute

Keywords: TiO_2; Binary nanofluid; Dispersion stability; Sedimentation; Nanotube; Nanosheet

1. Introduction

Nanofluid refers to a novel kind of two-phase suspension with addition of small amounts of metallic or nonmetallic nanoparticles with diameters from 1 to 100nm in the base fluid, which was proposed by Choi in 1995 [1]. In about two decades, a large amount of experimental and theoretical researches have been performed and advantages of nanofluids including high thermal conductivities, subcooling degree reductions in thermal energy storage etc. were demonstrated adequately. Nevertheless, poor dispersibility and stability are still challenges of all research. Because nanoparticles suspended in base fluid possess

* Corresponding author. Tel.: +86 20 39322581; fax: +86 20 39322581.
E-mail address: chenying@gdut.edu.cn.

Peer-review under responsibility of Applied Energy Innovation Institute
doi:10.1016/j.egypro.2015.07.282

large specific surface areas and high surface energy, which make nanoparticles easily aggregate and precipitate subsequently in short period of time.

Ultrasonic dispersion, mechanical dispersion, dispersant or surfactant addition and nanoparticle surface modification are effective methods to improve stability of nanofluids. However, the disadvantages of these methods are obvious. Long time ultrasonic dispersion could easily result in temperature increase, thereby lead to further aggregation as Brownian motion of nanoparticles will be more drastic and the collision frequency increase at high temperature. Impurity could be introduced in mechanical dispersion because strike and grind between metallic balls and canister could generate other substance, which affect impurity and property of nanomaterials. Dispersant addition could reduce effective thermal conductivity of nanofluids. Wang et al. [2] showed that the thermal conductivity enhancement reduced from 10% to 1.0% for Al_2O_3-H_2O and from 12% to 2.5% for Cu-H_2O nanofluids when SDBS weight fraction increased from 0.03% to 0.15%. Wusiman et al. [3] and Xie et al [4] found that dispersant addition could negatively affect thermal conductivity enhancement of CNT-H_2O nanofluids. Nanoparticles surface modifications are usually reacted in strong acid or alkali conditions and could easily damage thermophysical properties of nanoparticles during chemical reaction and the treatment processes are generally complex.

Mixing of nanoparticles of different shapes is a novel method to improve dispersion stability. Sun et. al [5] reported the experimental observation of dispersion tuning ligand-free ZnO quantum dots down to the single-particle level in polymer matrices through the use of exfoliated ZrP nanoplatelets and revealed that presence of exfoliated ZrP nanoplatelets could effectively disperse ZnO quantum dots within polymer matrices. Liu et. al [6] stabilized the TiO_2-H_2O nanofluids through the use of ultrathin ZrP nanoplatelets. Stability of nanofluids of nanoparticles mixture with different shapes of same material was less reported previously, but it is important for the study of the mixing effect on nanofluid stability.

In this research, binary aqueous TiO_2-H_2O nanofluids of different concentrations were prepared by dispersing certain amount of both TiNTs and TiNSs in deionized water. TiO_2 was employed as nanomaterial because the excellent photocatalysis properties and high thermal conductivity of TiO_2 have been widely researched and accepted [7]. Stabilities of binary nanofluids were observed visually and sedimentation heights variations with time were measured. Depletion forces were applied to interpret the results. To our best knowledge, the same or similar results have never been reported at present.

Nomenclature

H_0	height of nanofluid
H_1	Sedimentation height in stable nanofluid
H_2	Sedimentation height in unstable nanofluid
k_1	Sedimentation height ratio of H_1 to H_0
k_2	Sedimentation height ratio of H_2 to H_0

2. Experimental methods

2.1. Synthesis of TiNTs and TiNSs

The common hydrothermal synthesis method [8, 9] was used in TiNTs and TiNSs synthesis. The TEM (JEM-1200EX) image of TiNTs is demonstrated in figure 1 a. The diameters of TiNTs are approximately

10nm and the length reached to hundreds nanometers. The TEM (JEM-1200EX) image of TiNSs in figure 1 b showed that the TiNSs are generally square with the edge length in the range of 40 – 80 nm.

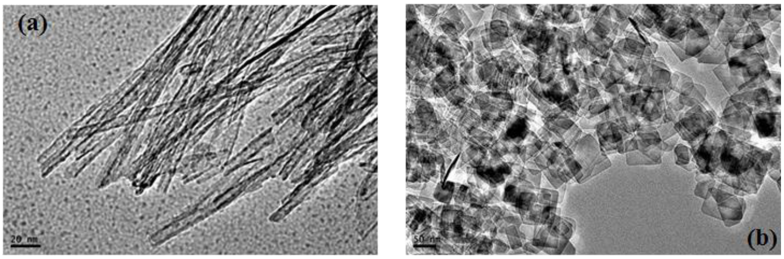

Fig. 1. (a) TEM image of TiNTs; (b) TEM image of TiNSs

2.2 Preparation of TiO_2-H_2O nanofluids

A certain amount of mixed TiNTs and TiNSs powder was added into deionized water. The resulting suspensions were stirred using a magnetic stirrer for 30 minutes to make the powder well suspended in water, and maintained in ultrasonic agitation for 1 hour using an ultrasonic cleaner to further improve the stability. Several TiO_2-H_2O nanofluids of different concentrations containing TiNTs as well as TiNSs were prepared. Five different mass fractions of nanofluids including 0.2 wt. %, 0.4 wt. %, 0.6 wt. %, 0.8 wt. % and 1.0 wt. % were prepared in this experiment.

2.3 Definition of stable and unstable nanofluids

The TiO_2-H_2O nanofluids samples of different concentrations and concentration ratios of TiNTs to TiNSs were observed visually 1 hour later after preparation. If nanoparticles keep suspended and no obvious sedimentation occur, as demonstrated in figure 2 (a), these samples were defined as stable samples; if nanoparticles obviously precipitate, as demonstrated in figure 2 (b), the samples were defined as unstable samples.

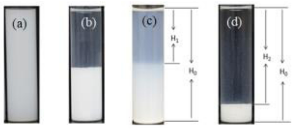

Fig. 2. Pictures of stable nanofluid (a) versus unstable nanofluids (b) and sedimentation heights of stable nanofluid (c) versus unstable nanofluid (d).

2.4 Sedimentation height measurement of nanofluids

Pictures of nanofluids were taken at certain time and demonstrated in figure 2 (c) and (d). The heights of nanoparticles sedimentation were measured by software Photoshop®. The sedimentation height ratios of stable and unstable nanofluids were defined as formula (1) and (2), respectively. The figures of height ratio variation with time were built and all data were fitted to determine the relative sedimentation velocities of nanoparticles.

$$k_1 = \frac{H_1}{H_0} \tag{1}$$

$$k_2 = \frac{H_2}{H_0} \tag{2}$$

3. Results and discussions

Stable and unstable nanofluids of different total concentrations and different concentrations of TiNTs are demonstrated in table 1. The total concentration of nanofluids was denoted as mass fractions of TiNTs plus that of TiNSs. As shown, the unitary TiNTs nanofluids were stable but unitary TiNSs nanofluids were unstable. Nanofluids containing both TiNTs and TiNSs were stable at high TiNTs ratios but were unstable at high TiNSs ratios.

Table 1. Stable nanofluids and unstable nanofluids.

Total (TiNTs and TiNSs) Concentration （wt. %)	TiNTs (wt. %)									
	Stable nanofluids					Unstable nanofluids				
0.20	0.20	0.16	0.14	0.12	0.10	0.08	0.06	0.04	0.02	0
0.40	0.40	0.32	0.30	0.28	0.26	0.22	0.15	0.10	0.05	0
0.60	0.60	0.50	0.45	0.40	0.35	0.32	0.30	0.20	0.10	0
0.80	0.80	0.60	0.55	0.50	0.45	0.42	0.30	0.20	0.10	0
1.00	1.00	0.80	0.70	0.60	0.55	0.52	0.45	0.15	0.05	0

The effect of the ratio of TiNTs to TiNSs on the stabilities of the nanofluids was studied. The sedimentation graphs of stable and unstable nanofluids of 0.1 wt. % and 1.0 wt. % total concentration are showed in figure 3. The sedimentation velocities are significantly relative to concentration ratio of TiNTs to TiNSs as well as total concentration. For stable 0.1 wt. % nanofluids, the sedimentation velocities of nanofluid containing only TiNTs are greater than those containing both TiNTs and TiNSs. The TiNTs nanofluids completely precipitated after about 7 days while the sedimentation height ratios of nanoparticles in binary nanofluids were only approximately 0.5 after 15 days. For unstable 0.1 wt. % nanofluids, both TiNSs nanofluids and binary nanofluids precipitate fast and all samples totally precipitate after 30 minutes, and the sedimentation height ratio k_2 vary with time nonlinearly. For stable 1.0 wt. % nanofluids, sedimentation velocities of TiNTs nanofluids and binary nanofluids are much slower than those of 0.1 wt. % nanofluids. The 1.0 wt. % TiNTs nanofluids precipitate completely after 13 days. Binary 1.0 wt. % nanofluids precipitate slowly within 15 days, and sedimentation velocity of nanofluids containing 0.9 wt. % TiNTs and 0.1 wt. % TiNSs is a little greater than that containing 0.7 wt. % TiNTs and 0.3 wt. % TiNSs. For unstable nanofluids of 1.0 wt. % nanofluids, the sedimentation velocities decrease with increased mass fractions of TiNSs. The 1.0 wt. % TiNSs nanofluid has the minimum sedimentation velocity and nanofluid of 0.5 wt. % TiNTs and 0.5 wt. % TiNSs has the greatest velocity. Stabilities of stable binary nanofluids when concentration ratios of TiNTs to TiNSs are in suitable range are better than those of nanofluids containing only TiNTs or TiNSs at the same total concentration. But sedimentation was greatly accelerated and stabilities were seriously deteriorated for other concentration ratios of TiNTs to TiNSs.

Zeta potential values and average particle sizes of 1.0 wt. % stable nanofluids of different concentration ratios were measured 1 hour later after preparation and shown in table 2. As the zeta potential values are higher and the average nanoparticles sizes of the binary nanofluids are smaller than that of the TiNTs nanofluid, the nanoparticles in binary nanofluids are less aggregated due to greater electronic repulsion interaction and the stabilities of binary nanofluids are better than the TiNTs nanofluid.

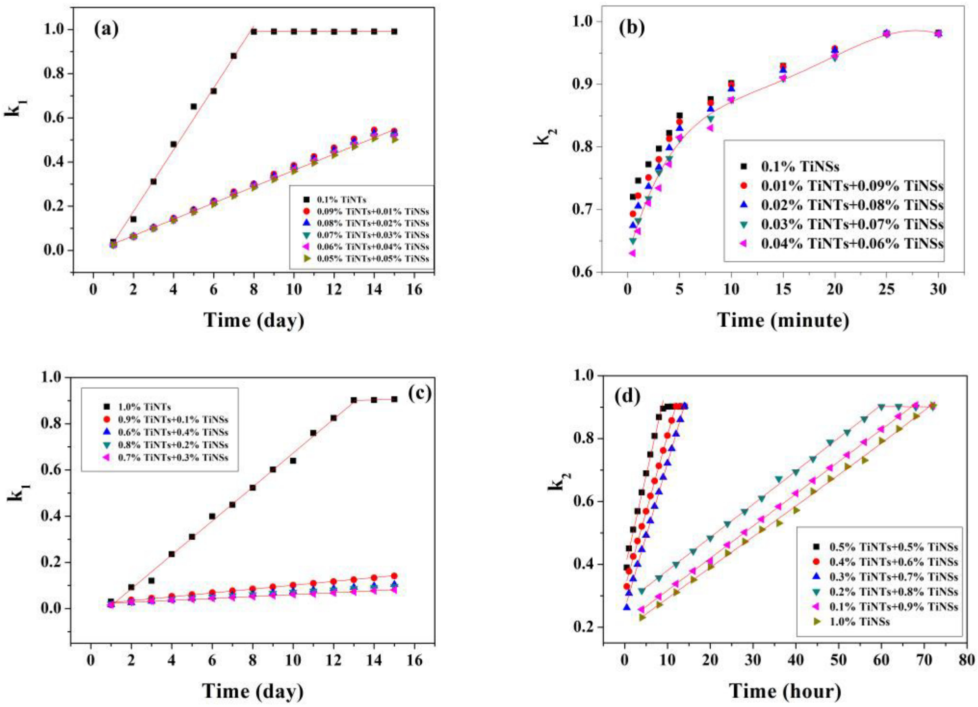

Fig. 3. Sedimentation graphs of (a) 0.1 wt. % stable nanofluids; (b) 0.1 wt. % unstable nanofluids; (c) 1.0 wt. % stable nanofluids; (d) 1.0 wt. % unstable nanofluids

Stabilities of unstable nanofluids may be related to depletion attractions. Nanoparticles of different shapes could introduce depletion interaction when being suspended in fluid [10, 11]. TiNTs will aggregate because strong depletion attraction are introduced when sufficiently high concentration TiNSs are added. TiNTs agglomerates will precipitate due to gravitational force after aggregating to large clusters, which could accelerate TiNSs sedimentations. Nanofluids stabilities are deteriorated seriously.

Table 2. Zeta potential value and average particle size

Mass fraction	Zeta potential (mV)	Average particle size (nm)
1.0 wt.% TiNTs	-35.82	239
0.8 wt.% TiNTs + 0.2 wt.% TiNSs	-42.46	151
0.6 wt.% TiNTs + 0.4 wt.% TiNSs	-41.22	144

Sedimentation velocities of nanofluids of different total nanoparticles concentration are concerned with viscosity. The viscosity of nanofluids increases with concentration [12]. Sedimentation velocities of 1.0 wt. % nanofluids are lower than those of 0.1 wt. % nanofluids due to higher viscosity of 1.0 wt. % nanofluids.

4. Conclusions

Stabilities of TiO_2-H_2O binary nanofluids were studied in this research. The preliminary results revealed that stability of binary nanofluid is concerned with concentration ratios of TiNTs to TiNSs and total concentrations of nanofluids. Stability of binary nanofluid is much better than that of nanofluid containing only TiNTs or TiNSs at same concentration when concentration ratio of TiNTs to TiNSs is in suitable range. Sedimentation could be greatly accelerated and stabilities are seriously deteriorated when concentration ratios of TiNTs to TiNSs are out of the stable range. We consider that the phenomenon is possibly related to electrostatic repulsion and depletion interactions in binary nanofluids. The mechanism of binary nanofluids stabilities needs further research.

Acknowledgements

We gratefully acknowledge the financial support provided by the Natural Science Foundation of China (NSFC) through contract NO. 51376050 and the Guangdong Natural Science Foundation through contract NO. S2013020012817.

References

[1] Das S K, Choi S U S, Patel H E. Heat transfer in nanofluids—a review[J]. Heat Transfer Engineering, 2006, 27(10): 3-19.

[2] Wang X, Zhu D. Investigation of pH and SDBS on enhancement of thermal conductivity in nanofluids[J]. Chemical Physics Letters, 2009, 470(1): 107-111..

[3] Wusiman K, Jeong H, Tulugan K, et al. Thermal performance of multi-walled carbon nanotubes (MWCNTs) in aqueous suspensions with surfactants SDBS and SDS[J]. International Communications in Heat and Mass Transfer, 2013, 41: 28-33.

[4] Xie H, Yu W, Li Y, et al. Discussion on the thermal conductivity enhancement of nanofluids[J]. Nanoscale research letters, 2011, 6(1): 124. 481-485.

[5] Dazhi Sun, W. Neil Everett, Minhao Wong, et. al. Tuning of the Dispersion of Ligand-Free ZnO Quantum Dots in Polymer Matrices with Exfoliated Nanoplatelets[J]. Macromolecules,2009, 42(5): 1665–1671.

[6] Liu Zhuowei, Chen Ying, Mo Songping, et. al. Stability of TiO_2 Nanoparticles in Deionized Water with ZrP Nanoplatelets[J]. Journal of Nanoscience and Nanotechnology,2015, 15(4): 3271-3275.

[7] Ni M, Leung M K H, Leung D Y C, et al. A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production[J]. Renewable and Sustainable Energy Reviews, 2007, 11(3): 401-425.

[8] Mogilevsky G, Chen Q, Kulkarni H, et al. Layered nanostructures of delaminated anatase: Nanosheets and nanotubes[J]. The Journal of Physical Chemistry C, 2008, 112(9): 3239-3246.

[9] Chen J S, Lou X W. Anatase TiO_2 nanosheet: An ideal host structure for fast and efficient lithium insertion/extraction[J]. Electrochemistry Communications, 2009, 11(12): 2332-2335.

[10] Mason T G. Osmotically driven shape-dependent colloidal separations[J]. Physical Review E, 2002, 66(6): 060402.

[11] Zhang J, Lang P R, Meyer M, et al. Synthesis and Self-Assembly of Squarelike $PbCrO_4$ Nanoplatelets via Micelle-Mediated Depletion Attraction[J]. Langmuir, 2013, 29(15): 4679-4687.

[12] Mahbubul I M, Saidur R, Amalina M A. Latest developments on the viscosity of nanofluids[J]. International Journal of Heat and Mass Transfer, 2012, 55(4): 874-885.

Ying Chen

Professor Ying Chen is from Faculty of Material and Energy, Guangdong University of Technology. Her research interests include heat transfer enhancement in cooling applications, thermophysical properties and phase change phenomenons of nanofluids.