CHARACTERIZATION OF PYSIO-CHEMICAL PROPERTIES OF NOVEL ONE STOP CHEMICAL METHOD IN PREPARATIONS OF COPPER NANOFLUIDS AND POSSIBLE EXPLANATIONS

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ABSTRACT

Nanofluid is a dilute suspension containing particles in nanometer sized which are dispersed in the base fluid like ethylene glycol or water. Nanofluid is one of the crucial discovery in modern science which found to be having better thermal properties compared with conventional fluids like water or ethylene glycol thus makes it ideal to be applied and utilized in many areas in heat transfer area such as cooling, utilized as fluid for heat echangers and etc. Besides, the nanofluid with the improved thermal properties could solve the problem faced by various industries in the area of heat transfer. For example, in the semiconductor industry, the needs of superior cooling coolant are very crucial.In this paper, presents about preparation of copper nanofluid using novel one stop chemical method by reducing copper sulphate pentahydrate using reduction agent which is sodium hypophosphite in ethylene glycol as base fluids. The obtained nanofluid by using this novel one stop method is more stable besides cheaper and faster compared with two stop method whereby in the two step method, the production of the nanoparticles and the nanofluids are isolated. The process of drying, storage and transportation of the nanoparticles that takes place in two step method have cause the agglomeration and sedimentation of the nanofluids. As the result, the agglomeration could cause the settlement and clogging in the microchannel besides reduce the thermal conductivity. Therefore in the novel one stop method the production of the nanoparticles and the nanofluids are combined and not separated to avoid the process of drying, storage and transportation of nanoparticles. Meanwhile the nanofluid that obtained were analyzed using Transmission Electron Microscopy (TEM), UV-Vis Spectrophotometer, Viscometer and Fourier Transform Infared Spectroscopy (FTIR). The effect and influences of pH and dilution to the reaction rate and properties of nanofluid were also investigated.

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CHAPTER 1

INRODUCTION

1.1 Background Of Study

There are some various problems faced by various industries worldwide due to the area of heat transfer. For example in semiconductor manufacturing, the needs of superior cooling coolant of computer chip are very desperate due to the limitations of already available cooling system. Meanwhile for chemical or oil and gas industries, the needs of material or substance having high thermal conductivity and at the same time capability of storing high heat energies also very viable to replace the already available materials that possessing low thermal conductivity as well as low heat energy capacitance. So in order to overcome those problem arising from the area of heat transfer, the nanotechnology field is emerging to overcome those problems not just for oil/gas or semiconductor but as well as various field of industry. Nowadays, nanotechnology is an very important field with billions spending on research alone in various sector in industries such as space, defense, medicine, energy, semiconductors, manufacturing company and etc. Nanotechnology is ways of developing materials at the level of atoms or molecular in order to make the materials possessed with certain electrical or chemical properties. For instance the development of nanofluid such as copper or iron nanofluid which is consist of nano particles and base fluid which is developed to increase the thermal conductivity and other chemical properties. Nanofluid is a suspension containing nano-scaled metallic or non-metallic totally suspended particles which are stabled within a solvent fluid. This superior heat transfer fluid is proved chemically and physically having great thermal conductivity and high storage heat capacity.

Furthermore, process of cooling or in other words heat removal system remains as one of the main concerns in various industries either semiconductors or manufacturing facilities, therefore remain as one of the main challenges faced by various industries. Because of the lack of heat transfer properties possesed by conventional fluids, the need of major improvements in cooling system need to be implemented although various research and development have been carried out to improve it. As a result, the usual solutions to overcome this problem arising for heat transfer rate is heat to increase the surface area of the heat exchanger which resulting to the design and fabrication of extremely huge heat exchangers or in other words, unacceptable increases in the size of heat exchangers. This cause significant increase in cost not only to built it but also significant increase in utility as well as the maintenance cost. Besides, higher power consumptions means higher rate of pollutions due to the increase of undesirable gasses discharged from the combustion of fuel or charcoal process. So alternative and efficient way to overcome those problem is the development of nanofluids.

High thermal conductivity in nanofluids which is higher than the conventional heat transfer fluid that normally used like water or ethylene glycol makes the nanofluid is very ideal for airplanes, machines and engines, reactors, heat exchanger units and other else. For an addition, before the introduction or development of nanofluid, there was a trial to increase heat transfer by using micron-sized particles dispersed in fluid but it was not successful because the fluid could cause clogging and sedimentation and also not efficient enough.(Xuan and Li, 2000).

Example of nanofluid which is made by dispersing nano particles in base fluid is 0.3 volume percent of nano particles are dispersed in ethylene glycol and the result is the thermal conductivity increase by up to 40 %. (Eastman and Choi 1995). However it is noticed that if we used the non-metal nano-particles like aluminum oxide (Al_20_3) or copper oxide (CuO) the amount of heat transfer increase is not as large as metal nano-particles. Therefore we can say that type of particles together with the amount of dispersed particles, material type and particle shape influenced the heat transfer enhancement and the thermal conductivity.

Recently, the nanofluids is prepared by dispersing Cu nanoparticles into the base fluid where the preparation of nanofluids and preparation of Cu nano particles done separately. This cause the agglomeration and sedimentation of the nanoparticles which caused the thermal conductivity to decrease and also settlement and clogging in microchannels. (Zhu et al 2004). For example Cuo nanoparticles when poured to reagent ethylene glycol, the particles sedimented within several minutes as the particles remain in clusters without being dispersed.(Kiyuel 2005). So to disperse the particles, sonication (20 kHz, 100W) is used for about 9 hours and the result is the particles average size is approximately 60 nm which is about 5 times larger than the each particle. (kiyuel 2005). If the sonication duration is too long it is proven experimentally that the particles will get coalesced again. So between 1-30 hours tested, 9 hours is proven to be theoptimum duration of sonication. (Kiyuel 2005)

So because of that, it is necessary to develop one stop chemical method that combine both the preparation of nanofluids and the preparation of nanoparticles to avoid the agglomeration and sedimentation of the nanoparticles besides reduce the production cost. (Zhu et al 2004). So finally the novel one stop chemical method to prepare copper nanofluids have been developed whereby reducing $CuSO_4.5H_2O$ with $NaH_2PO_2.H_2O$ in ethylene glycol under microwave irradiation. The result shows that the copper nanoparticles size should be in between 10-20 nm and the less the size the better the stability and the nanofluids prepared. Besides, the nanofluid that have been prepared using this method is stable for more than 3 weeks in the stationary state while managed to last for about 8 h under centrifugation at 4000 rpm without sedimentation. (Zhu et al 2004). However, the thermal conductivity of the particles used also should be higher to obtain better nanofluids with better thermal conductivity. Copper is used because the thermal conductivity is 402.5 W/m.k which is quite higher than its rival like aluminium (237 W/m.k) and etc. So as the conclusion the purpose of this research are to study and understand the characterization of novel one stop chemical method in preparation of copper nanofluids.

1.2 Problem Statement

The conventional heat transfer fluid that widely used like water and ethylene glycol are no longer suitable to used in heat transfer or thermal conductivity purpose of heat transfer or thermal conductivity area and have been a barrier for industries. So alternative fluid must been developed which should have high thermal conductivity as well as large energy capacitance or energy storing capabilities. So nanofluid have been developed to overcome those arising problem. However the preparation of nanofluid have been an issue where the already available method which isolates the preparation of both nanoparticles and nanofluid caused the agglomeration, sedimentation, clogging and other problems. This caused the thermal conductivity and heat transfer rate decreased. So a novel one stop chemical method should developed which combined the preparation of both nanoparticles as well as nanofluid in single step to overcome those problems. Other problem statements of this research are :

2. To calculate and study the physical properties of nanofluid like thermal conductivity, viscosity, density and other else.

3. To study the effect of using different concentration or volume fraction to prepare the nanofluids.

Objective

The objective of this research is to study the characterization of physicochemical properties of novel one step chemical method for preparation of copper nanofluids whereby alternating manipulating variables like copper sulphate pentahydrate, addition of surfactant and other external factors to the nanofluid obtained and study the physical properties like thermal conductivity.

1.3 Scopes of Study

The scopes of this research are studying and implementing techniques to obtain more stable copper nanofluid (time taken for the nanoparticles to agglomerate or sedimenting) as well as obtaining highest thermal conductivity of copper nanofluid as possible. This techniques or properties includes variation in particle size , techniques of dispersing into larger area in fluid and at the same time reducing as much as possible the rate of agglomeration or sedimentation, the effectiveness or effect of using chemicals that avoid or reduce the agitation or sedimentation of nanoparticles to the thermal conductivity. Lastly the thermal conductivity can be calculated from the transient hot wire method (THW) or from the formula.

1.4 Rationale and Significant of study:

The rationale and significance of this study about the nanofluid is :

High specific area to have more heat transfer surface between particles and fluids.

As we know nanofluid which contains suspended nanoparticles contains nanoparticles in average size of 10-30nm which is very small. This increase the heat transfer surface area for more effective heat transfer hence reducing the energy loss.

Reduced particle clogging as compared to convention slurries so that process miniaturization could achieved. With implementing nanofluid, particle clogging can be reduced so the need for larger area of instruments or equipments are not necessary and hence miniaturization could be achieved which could reduced large amount of cost.

Reduced pumping power as compared to conventional liquid to achieve equivalent heat transfer. As we know the nanofluids containes nanoparticles have higher thermal conductivity as well as the capability of storing higher amount of energy. So more amount of energy removal could be achieved in same amount of conventional fluid. So the pumping power can be reduced resulting higher life span of instruments as well as the cost reducing for energy.

So as we can know the importance and significance of the nanofluid and its usage. Therefore in this research, we are going to prepare the nanofluid using one stop chemical method and studying its properties. Besides that we are also going to study the factors that influence the fluid stability by manipulating certain variables like concentration of the reactant, addition of surfactant and other chemicals like kerose. In other words stability means times taken for the particles to start agglomerating and also the higher area of dispersbility. The higher the time needed, the higher the stability of the nanofluid obtained.

CHAPTER 2

LITERATURE REVIEW

Nanofluid which contained nanoparticles either metallic or non metallic dispersed in a base fluid is proven theoretically and experimentally capable to increase the physical properties like thermal conductivity as well as the heat transfer properties. This cause a huge demand of the fluid in various industries as a replacement of the conventional heat transfer fluid like ethylene glycol and water which have low thermal conductivity with poor heat transfer properties. Due to its properties, the fluid is very suitable used as a coolant, implemented in heat exchanger where the area of the heat exchanger can be reduced due to the higher rate of cooling per m_2 compared with water, thus process miniaturization could be achieved and other various industries worldwide. Furthermore due to its higher and better thermal properties like thermal conductivity and heat capacity, compared with conventional fluids, the nanofluids could proven to be very ideal to be applied and utilized commercially in various kinds of applications and fields includes automotive, microelectronics, chemical industries as well as the other manufacturing industries.

Nanofluids with its nanometer sized of solid particles, fibers and tubes suspended in different kinds of base fluids like water, ethylene glycol and etc. are having superior thermal properties and excellent in enhancing heat transfer is because of several reasons includes the Brownian motion of the particles in the fluid, the effect of the particles size and other else. Furthermore, the nanofluids with its ultrafine particles size could flow smoothly in the microchannel without clogging and resulting to the miniaturization or reductions for the cooling device. So the need of the nanofluid is very crucial and the preparations of the fluid should be developed to commercialize the nanofluid to the needed industry.

Therefore, nanofluids that are prepared properly should have this kind of characteristics that shown below compared with conventional heat transfer fluids:

1. Having the surface area as high as possible to enhance the rate of heat transfer between the solid particles and the fluids.
2. Brownian motion of particles with high dispersion of particles in the fluids and having high stability.
3. Ability to achieve equal amount of heat removal with the conventional fluids with lesser pumping power when the nanofluids are utilized in the device like radiator.
4. Ability to reduce the particle clogging which results to the system miniaturization if compared with conventional slurries.
5. Enhancement of several magnitude of thermal conductivity where at least 40% minimum should be achieved when compared with its base liquids.
6. Better and superior in other thermal properties like heat capacity when compared with the conventional heat transfer fluids.

2.1 Two Step Method

However there are 2 different methods available to prepare the nanofluids which is two step methods and the other one is novel one stop chemical method. For the two step methods, the preparation of the nanoparticles and the nanofluid is done separately where the particles first produced as dry powder and later the nanoparticles poured into the base fluid in the second step and continued by using ultrasonic vibration or other necessary instruments to disperse the nanoparticles throughout the larger area of the fluid. Moreover, nanoparticles that produced with different routes will possess different morphologies, structures as well as different physical and chemical properties which later will effect and influence the stability and quality of the nanofluids. There are several routes are available currently to produce the nanoparticles like either using vapor, liquid or the mechanical routes. Simple example of mechanical routes used to synthesize the nanoparticles are such as milling and grinding which is a simple and straightforward but requires significant amount of energy. (Wen et al 2009). Meanwhile in the vapor phase route, the method like combustion, pyrolysis, plasmas, laser ablation, laser pyrolysis or chemical vapor decomposition are carried out to produce reactive vapor which resulting to the nucleation and growth occur. As an addition, the vapor-phase method are the most preferred way to produce ultrafine in terms of quality and cost, where it is the most preferred way for for large scale productions. Meanwhile in the liquid routes to produce the nanoparticles, method such as wet chemical method are involved in which chemical reactions of few reagents with one desired product but producing other undesired product or impurities which are difficult to removed completely. As the result, this will effect the quality and the performances of the nanofluids obtained later. Therefore, this remains as one of the weaknesses in producing the nanoparticles using liquid method. As an addition the two step method is the one used conventionally by the certain industries to prepare the nanofluid. This method has strong and identified weakness where it caused the agglomeration and sedimentation of nanoparticles especially due to the process of drying, storage, and transportation of nanoparticles. Therefore, it resulting to the clogging and settlement in microchannels and also decrease in the thermal conductivity. Besides that, according to Wen et al also, almost all nanoparticles are much larger in dimensions in the form of dried agglomerates due to the strong Van der Waals attractive forces. Meanwhile, in the two step methods, the rate or amount of sedimentation and agglomeration are heavily influenced with the ways of manufacturing, handling and storage of the nanoparticles. So as the result, the methods, selection of routes and process itself that involves in producing the nanoparticles should be carried out carefully with proper knowledge in the properties of the substance in order to obtain stable and quality nanofluids. Meanwhile after pouring the nanoparticles into the base fluids, the process of dispersing the particle should be carried out to disperse the particles uniformly throughout thebase fluids. The nanoparticles either oxides or non oxides have high tendency to remain in clusters upon mixing with the base fluids due to its high surface activity. So it is very necessary to disperse the large agglomerates of particles into smaller or primary particles. Furthermore, the uniform dispersion of the particles is the key elements that influence or effects the performances of the nanofluids in heat transfer properties as well as the stability of the nanofluids. The higher rate of agglomeration and sedimentation, the lower the quality and stability of the nanofluids. The process of dispersing is usually carried out using general equipments such as sonicator, ultrasonic bath, magnetic stirrers, high shear mixers, homogenizers as well as the bead mills. Moreover, the dispersing time and its intensity will significantly influence the dispersion effects. The agglomerates of the particles which are weakly bonded can be easily separated and broken into the normal size by high shearing. (Wen et al 2009). Besides, static repulsion as well as steric hinderence are also necessary to overcome the attractive Van der Walls forces between the particles to prevent the agglomeration and resulting to the stable suspension of nanofluids. (Wen et al 2009). Besides that, there are also reported use of stabilizers or surfactants both in two stop methods as well as in novel one stop method in producing the nanofluids. These stabilizers are used to establish stearic barriers among the nanoparticles to achieve higher dispersion and stability. In the two step methods, the stabilizers or surfactant is added to the base fluids and mixed before dispersing the nanoparticles into the base fluids. Besides that, the addition of stabilizers could reduce the surface tension and change the wettability and viscosity which later resulting significant changes in the flow and heat transfer behaviors.

Moreover, the nanofluids prepared without the stabilizers could be used instantly but the agglomeration and sedimentation will take place with time. Research have been done by Wen et al 2009 using dried alumina nanoparticles with particle size approximately 20nm as shown in Fig 1a to prepare the aluminium nanofluids without stabilizers.

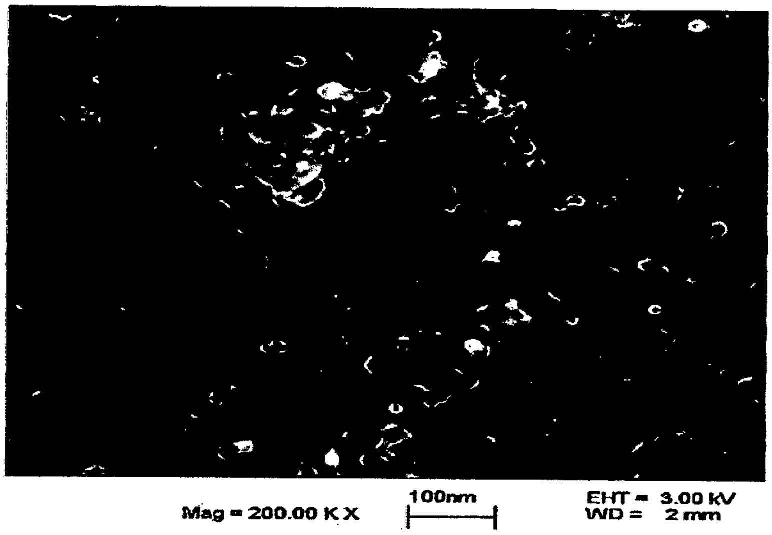

Figure 2.1: Dried alumina nanoparticles

As shown in Fig 1b below, the nanofluids become completely agglomerated and separated with its nanoparticles after several hours which is less than a day.

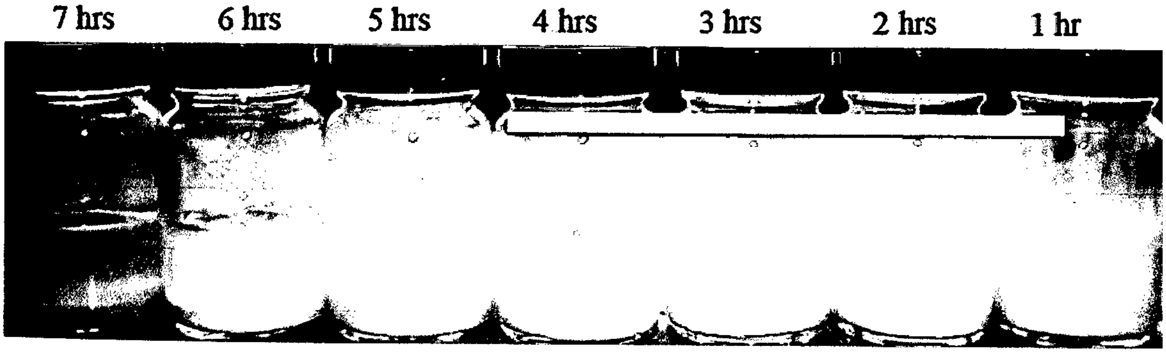

Figure 2.2: Al2O3 nanofluids (without any stabilizer) stability change with time

So ways to improve the stability of the nanofluid and also decrease the rate of agglomeration and sedimentation should be identified and developed if we want to use the second method to produce the nanofluid.

This method of preparing nanofluid is prepared by Hong et al (1998) by dispersing Ferum nanocrystalline powder in ethylene glycol to obtain Ferum nanofluid. Xuan et al (2001) prepared copper nanofluids by dispersing copper oxide (CuO) nanoparticles into base liquid which is water and oil. Murshed et al (2003) prepared Ti nanofluids by dispersing $Ti0_2$ powder into water. Xie et al (2004) prepared Al nanofluid by dispersing Al_20_3 nanoparticles into water, ethylene glycol separately. Meanwhile Patel et al (2003) have managed to prepared Ag and Au nanofluids by dispersing the Ag and Au nanoparticles respectively into the toluene as base liquids.

Table below summarizes the list of nanofluids that produced using single step methods as well as other details that are related :

Nanofluids	Synthesis Process	Particle Loading (Vol %)	Particle Size (nm)	Researcher
Cu/H2O	Two-step	7.5	100	Xuan et al, 2000
Ag/toluene	Two-step	0.001	60-80	Patel et al, 2003
Au/toluene	Two-step	0.00026	10-20	Patel et al, 2003
Au/ethanol	Two-step	0.6	4	Putnam et al, 2006
TiO2/H2O	Two-step	5	15	Murshed et al, 2005
Al2O3/H2O	Two-step	5	20	Xie et al, 2002
Al2O3/EG	Two-step	0.05	60	Xie et al, 2002
CuO/H2O	Two-step	5	33	Zhang et al, 2006
SiC/H2O	Two-step	4.2	25	Xie et al, 2001
NCTs/engine oil	Two-step	2.0	20-50	Lie et al, 2005
NCTs/poly oil	Two-step	1.0	25nm × 50μm	Choi et al, 2001
NCTs/EG	Two-step	1.0	15 × 30μm	Xie et al, 2003

Table 2.1 Nanofluids produced using two step method

2.2 Novel One Stop Method

Meanwhile for the preparation of nanofluids in single step or one-stop method is the combination of preparing nanoparticles and the nanofluid at the same time. This method could skip and avoid process of drying, storage and transportation that have been proven degrade the performance of the nanofluid by agglomeration and sedimentation activity. Single step method can be divided into 2 main method which is physical method and chemical method. In physical method, Choi et al (1999) has developed one stop physical method in which Cu vapor is directly condensed into nanoparticles by contact with a flowing low-vapor pressure liquid which is ethylene glycol. Although the nanofluid obtained is stable with nonagglomerating and sedimentated particles, however this method is not economical and have limitations in which only low vapor pressure liquid can be used. Meanwhile the single step or one stop chemical method is developed by Zhu et al (2004) by reducing copper sulphate pentahydrate which is a source for the nanoparticles with sodium hypophosphite as reducing agent under microwave irradiation. The result is very stable nanofluid with non agglomerating particles or sediment. The stabilization of the Cu nanofluid obtained is better than that of the one prepared by a step by step method. This is because the fluid is stable for more than 3 weeks in the stationary state, 2 weeks and more in the stationary state at 120 °C and more than 8 h under centrifugation at 4000 rpm without sedimentation compared with the one prepared by step by step method or in other words two step methods.

Therefore when compared the two step methods with the novel one stop chemical methods, it is obvious that the outcome or result from the one stop methods are unexceptionally better than the two step methods. The obtained nanofluids from single stop methods possessing better stability with minimum or less agglomeration or sedimentation which serves as the main concerns in determining the quality of the nanofluids and also its performances in the heat transfer properties. Therefore, the nanofluids also could achieve higher thermal conductivity, heat capacity and other thermal properties than the nanofluids from step by step methods. Although the performances of nanofluids by one stop chemical methods is unquestionable when compared with the nanofluids from step by step methods, however there are one disadvantages that have been identified according to Wen et al,2009 where there are still residual reactants that still left in the nanofluids after reaction completed from the incomplete reaction or stabilitzation. For instance lets take the copper nanofluids sysnthesized using novel one stop method by Zhu et al 2004 by reducing copper sulphate pentahydrate with reduction agent which is sodium hypophosphite. After reaction completed, there are still residual or balance of sodium hyphophosphite which are traceable using several analytical equipments which will be discussed later in the upcoming chapter. The copper sulphate pentahydrate acts as limiting reactants while the sodium hyphophosphite serves as excess reactant. Besides that, according to several researchers, the two step method remains as the best methods in systhesizing the nanofluids for metal oxide nanoparticles. Moreover, there are very few findings or research carried out successfully in synthesizing the nanofluids using novel one stop chemical method as compared with its rival. Meanwhile there are great number of research that have been done in preparing the nanofluids using step by step method. This is maybe due to the high availability of the ultrafine nanoparticles that could be purchase or bought easily as well as very little efforts in synthesizing the nanofluids where the nanofluids can be prepared easily by pouring the nanoparticles into the base liquid followed by dispersing process. So as the most suitable technique or method to prepared the nanofluid which having better stability and superior thermal properties is this method which is called novel one-stop chemical method in preparations of copper nanofluid.

Some of the previous research done in synthesizing the nanofluids using novel one stop method includes Akoh et al which had developed direct evaporation approach called the VEROS (Vacumm Evaporatiòn onto a Running Oil Substrate) technique. In this research, the expected outcome is to produce nanoparticles however to separate the nanoparticles from the fluids itself are difficult. Wagener et al has developed modified VEROS process where high pressure magnetron sputtering for the preparation of nanofluids with dispersion of metal nonoparticles such as Ag and Fe. Besides that, later Eastmen et al had also developed a modified VEROS technique by condensing the Cu vapor into nanoparticles and contacting it with a flowing low-vapor pressure of Ethylene Glycol. Zhu et al have developed novel one stop chemical method in preparing copper nanofluids by reducing copper