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Synthesis and Characterization of Doped Nano Heat Transfer Fluid for Concentrated Solar Power Plant

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Abstract: With the view to minimize the energy crisis due to the ever depleting non-renewable energy resources, this research aimed to apply nanotechnology to enhance the efficacy of solar energy power plant – a renewable energy resource. According to literature Concentrated Solar Power Plant system requires heat transfer fluid (HTF) for proficient working. This research reports the synthesis of novel, efficient heat transfer fluid doped with nano sized particle including carbon nanotubes and metal oxide i-e copper oxide. This nano heat transfer fluid (NHTF) has very low melting point in comparison to conventionally prepared molten salt mixture for heat transfer purpose which typically have high melting point characteristically 140°C or higher. Most prominently this NHTF has enhanced thermo-physical properties including high thermal stability and high specific heat capacity. These properties ensures effective increase in thermal energy storage (TES) which is a key factor in solar thermal power plant and make it broad range operating heat transfer fluid.

Keywords: Eutectic, Nano Heat Transfer Fluid, Specific Heat Capacity, Concentrated Solar Power

1. Introduction

Energy is an ultimate irreducible essence of the universe without which life cannot be imagined but today world is facing an acute energy crunch. Global energy demand is continuously escalating manifolds due to the fast pace of technological advancements and unequal demographic distributions. The world's total electricity consumption in the year 2000 was 14,396 TWh which is predicted to rise to 27,335 TWh by 2020 [1]. This serious energy crisis is mainly attributed to the continuous dependence on fossil fuels which results in the exhaustion of natural non-renewable resources. In addition, the burning of fossils fallout in high carbon dioxide emissions adding to the ever increasing green house gases which ultimately results in global warming. Presently top priority of developed countries is exploiting the use of clean renewable energies so as to seek sustainable development because these resources cause less environmental impact. Modern nanotechnology provides new opportunities and is expected to play considerable role in reviving the traditional energy industries and invigorating the rising renewable energy industries [2, 3].

Apart from other innumerable applications of nano-technology, in the field of energy conservation its use in increasing the efficiency of Solar Power plants by enhancing the heat transfer properties is now gaining momentum. With the aid of nanotechnology, such fluids can be synthesized which proper heat transfer within a system. Solvents doped with nanoparticles at minute concentration are termed as nanofluid, a term proposed 1995 [4, 5]. Nanofluids are exemplified as next generation heat transfer fluids as they proffer new exciting possibilities to embellish heat transfer performance in comparison to pure base fluid. These fluids are required to have remarkable and finer thermo-physical properties than conventionally used heat transfer fluid and also the slurries containing milli and micro sized particles The dispersion of milli and micrometer sized particles is prone to sedimentation and clogging in micro-channels. Due to settling problems there is lack of stability of suspensions, which tempt additional flow resistance and possible erosion [6, 7]. Properly engineered thermal nanofluids possess number of benefits such as nanometric particles have fairly large surface area which not only aids in improving heat transfer capabilities but also significantly improve stability of suspension. Small size of nanoparticles perks up the abrasion-related properties. Successful employment of nanofluids will result in reduced particle clogging and promoting system miniaturization. So using nanofluids for heat transfer application with enhanced thermo-physical properties allows its effective use in concentrated solar power plant [8].

Preparation of nanofluids is the first key step in experimental studies of nanofluids. Nanofluids are not simply liquid-solid mixtures, however special requirements are essential to prepare it, for example, stable and sturdy suspension, negligible agglomeration and clogging etc. So principally they are prepared by using two different methods commonly called as one-step method and two-step method [8, 9]. Enhancement in different thermo-physical properties is the basic mean to make potent and well operative heat transfer fluid.

A lot of work has been done on the thermal conductivity of nanofluids. Nevertheless very little research has been done on specific heat capacity but enhancment in specific heat capacity can make heat transfer fluid more effective [6]. As nanoparticles contribute significantly to the total heat capacity of the nanofluid while they go through a phase transition, during a first order phase transition heat capacity of substance enhances manifold and due to the very large surface area of nanoparticles, the effect of surface charge can be significantly increased and as a result it results in over all stability of the resulting nanoparticle/liquid mixture [10]. Shin and Banerjee generated nanofluid by making suspension of silica in alkali chloride eutectic salt as basefluid and reported 14.5% enhancement in specific heat capacity for 1% concentration by weight [2]. Opposingly, Zhou *et al* found that the specific heat capacity of Al_2O_3 nanoparticles in water decreased by 40–50% at 21.7% volume concentration of Al_2O_3. Most obvious reason for such behavior might be agglomeration of particles [8].

The aim of this research work was to synthesize NHTF for the application of concentrated solar power plant and to study the effect of nanopaticles on the properties of NHTF.

2. Materials and Method

All the chemicals were purchased from Sigma-Aldrich, Germany except the multi walled carbon nanotubes (MWCNTs) which were manufactured through Chemical Vapor Deposition (CVD) method by patented method [3].

Step 1: Synthesisof eutectic mixture

Eutectic salt mixture of $NaNO_2$: KNO_3: $LiNO_3$: KCl (28:45:25:2) was prepared by thoroughly mixing finely ground salts. Mixed salts were initially dried at 150°C to remove moisture.

Step 2: Synthesis of functionalized CNTs

Raw CNTs were purified in order to remove impurities before further processing. MWCNTs were heated up to 400°C for 15 minutes and then sonicated at 60°C for three hours in sonicator and diluted by water. Filtration of solution was carried out using membrane filter paper of pore s 0.45µ using a suction filter apparatus and washed up to neutral pH, then dried at 100°C for 4 hours. The purified MWCNTs were treated with a mixture of sulfuric acid and nitric acid (3:1) and sonicated for 8 hours at 60°C. The acid treated MWCNTs were again diluted and followed by filteration and drying.

Step 3: Synthesis of copper oxide nanoparticles

Sol-gel process was used for CuO nanoparticles production, 10 gm of $Cu(NO_3)_2.H_2O$ is dissolved into 40 mL of ethanol. It was stirred for 1 hour to obtain the homogeneous solution. and kept for 24 hours so that to allow it to form gel, it was dried at 170°C and pulverized and calcinated at 300°C for one hour.

Step 4: Preparation of nanofluid

0.4 and 0.8 wt % of each MWCNTs and CuO nanoparticles were added in 0.025% Sodium Dodecyl Sulphonate (SDS) surfactant solution. 1 gram of eutectic mixture is added to each of MWCNTs and CuO solution. These solutions were strongly stirred for at least one hour followed by sonication of MWCNTs and CuO sample for half an hour and 15 minutes, respectively. It was observed that on increasing the time of sonication nanoparticles start to segregate. Obtained homogenous dispersion was subjected to drying on hotplate at 60°C. Samples were again dried in an oven at low temperature to ensure complete removal of moisture.

3. Characterization

Melting point was measured by using melting point apparatus (R000105152 Bibby Scientific Limited). Crystal modality is vital for nano materials. XRD pattern of sample was analyzed with X-ray diffractometer (Philips X'Pert PRO 3040/60) employing Cu-Kα radiation. Scanning Electron Microscopy (SEM) Analysis was carried out for morphological studies and was performed using LEO 1530 FEG-SEMEDS. The specific heat capacities of all the materials have been calculated by using DSC results. DSC/TGA analysis was carried out using instrument (SDT Q.600 TA Instruments, Inc.) equipped with computer for control and data handling. The temperature was ramped from 50 to 700°C at 10°C/min.

4. Results and Discussion

The present study was carried out to synthesize nano heat transfer fluid with enhanced thermo-physical properties i.e low melting point, high thermal stability and high specific heat capacity for effective use in concentrated solar power plant system as solar light absorber.

4.1. Melting Point Analysis

Ideally the material used for heat transfer purpose must be liquid at room temperature and conventionally liquid material such as water, mineral oil etc are used but they have low boiling points which make it unsuitable for CSP functioning. In this research heat transfer fluid was developed as a result of material screening process, in order to achieve low melting point (so minimum amount of energy is used to convert it into fluid form), eutectic salt mixture was prepared and tested for melting point measurement. It is found that addition of nanoparticles do not alter the melting point of eutectic salt mixture. Melting point of prepared sample was very low i.e 60°C in comparison to literature.

The mechanism of lowering melting point by making different eutectic mixture can be attributed to the fact that this mixture tend to disrupt intermolecular forces i-e reducing the variation in enthalpy or to increase the disorder generated upon melting, this lead to melting point reduction [11, 12].

4.2. XRD Studies

To be ensure about proper synthesis of nanomaterial, XRD of carbon nanotubes and CuO was carried out to look at its crystal structure. The diffraction peak could be attributed to existence of amorphous MWCNTs as depicted by Figure 1a. An XRD spectrum for CuO is shown in Figure 1b which exhibit Braggs reflection at about 32°, 35°, 39°, 48° 53°, 58°, 61°, 66°, 68°, 72° and 75° degrees corresponding to 110, 111, 111, 202, 020, 202, 113, 311, 220, 311, 004 confirming the crystal planes of CuO nanoparticles [13]. The average crystalline size of copper oxide was estimated by using Scherrer formula which is equal to 27.76 nm.

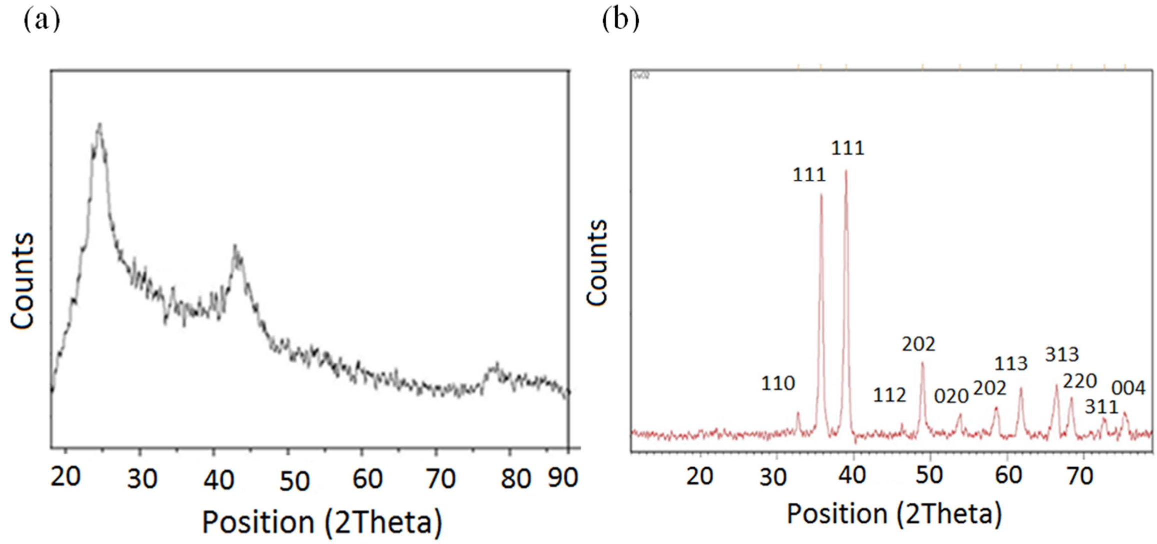
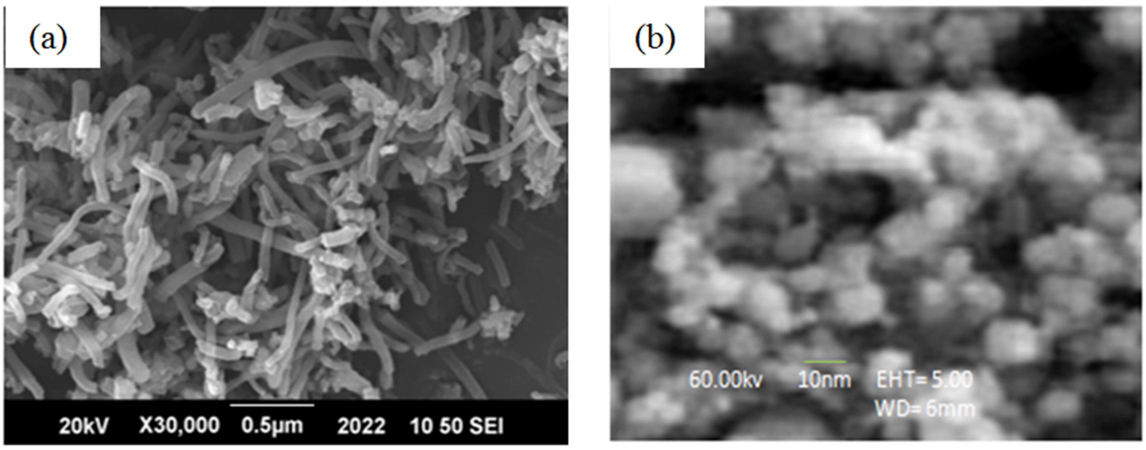


Figure 1. *X-Ray Diffraction pattern of (a) functionalized MWCNTs (b) CuO nanoparticles.*

4.3. SEM Analysis

The micrographs of functionalized MWCNTs, CuO, MWCNT doped nano heat transfer fluid, CuO doped nano heat transfer fluid as shown in Figure 2(a-d). It is clearly depicted by the SEM micrographs for functionalized MWCNT that MWCNTs have a diameter in the range of 35-50 nm and also they are de-agglomerated having a clean surface which confirms an effective purification and oxidation treatment [14] and CuO particles are spherical in nature and also not agglomerated. SEM micrographs show its particle size is between the range 25-30nm.



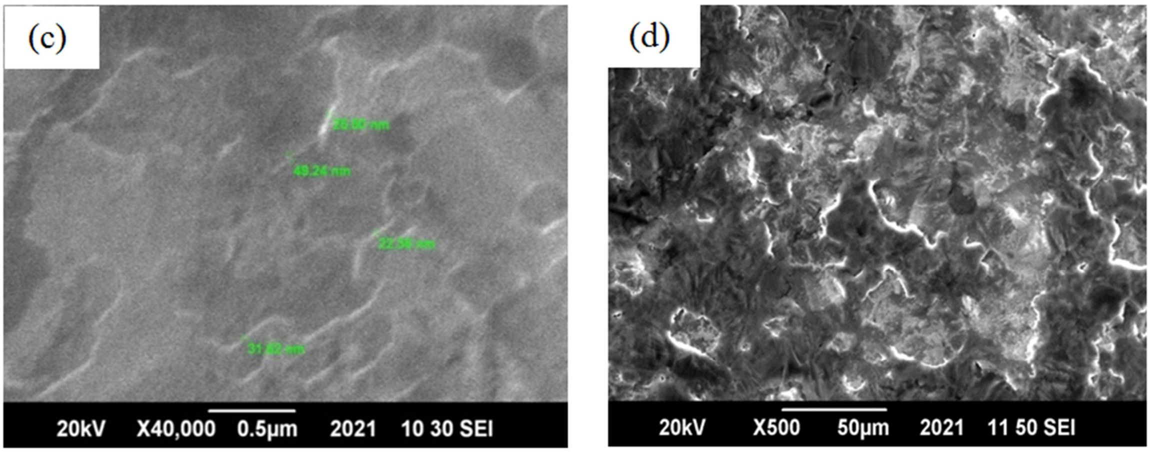


Figure 2. *SEM micrographs for (a) MWCNTs (b) CuO (c) MWCNTs doped nano heat transfer fluid (d) CuO doped nano heat transfer fluid.*

4.4. Thermal Stability

High thermal stability of heat transfer fluid is the basic requirement and one of most important parameter to make it operative at high temperature in CSP system. The TGA curve clearly proves the thermal stability of the material at higher temperature. The material does not suffer any significant weight loss till the temperature as high as 600°C as shown in Figure 3. The minimal weight loss that appears may be because of the moisture [11, 12]. However beyond 600°C thermal degradation of material starts rapidly till 800°C. Thermal stability analysis of eutectic mixture shows that nitrates of alkali metals are quiet stable at elevated temperatures as high as 600°C [13, 14]. The mechanism behind its stability was that as temperature gradually increases nitrate decomposes at high temperature at first and then the decomposition rate of nitrates was slower than the oxidation of nitrites [15]. Therefore thermal stability of nanofluids is mainly because of proper composition of eutectic mixture.

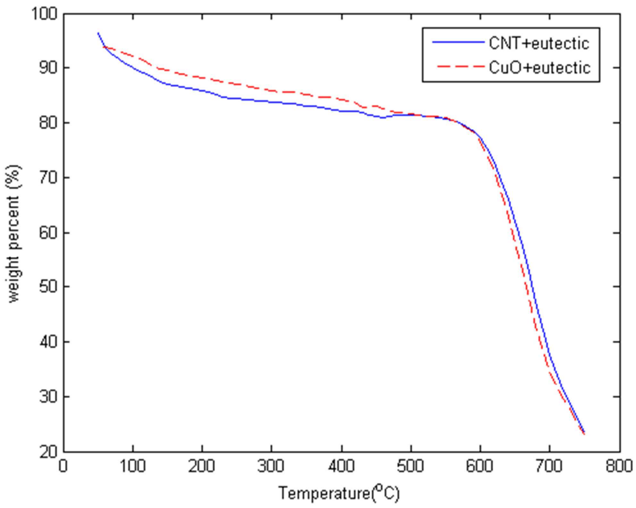


Figure 3. *TGA curve showing thermal stability of nano heat transfer fluid.*

4.5. Specific Heat Capacity Analysis

In order to calculate heat capacity following formula is used: [11, 15]

$$Cp = \frac{Q}{m\Delta T} \qquad (1)$$

Where; Cp = Specific heat, Q = Heat flow, m = mass, ΔT = Change in temperature

The enhancement in specific heat capacities of NHTF (containing different percentages i.e. 0.4%, and 0.8% of both multi walled carbon nanotubes and CuO nanoparticles has been observed as shown in Figure 4(a-b). It clearly shows that nanofluids have higher specific heat capacity than undoped material. The anomalous increase the specific heat capacity of nanofluid can be justified as follows; As nanoparticles have a greater surface area per unit volume than larger particles i-e within nano dimension the amount of atom exposed at surface is tremendously high than that of bulk material [15].

This high surface area results in high rate of reaction in the form of absorption of heat, leading to over all higher surface energy (Kinetic energy). Moreover; larger surface area cause increase in thermal resistance between the solid nanoparticles and fluid particles of molten salt mixture [15, 16]. This thermal resistance provides the additional thermal energy storage in the form of increased specific heat capacity [17]. Moreover, the surface energy of whole system increases resulting in effective enhancement in specific heat capacity [18].

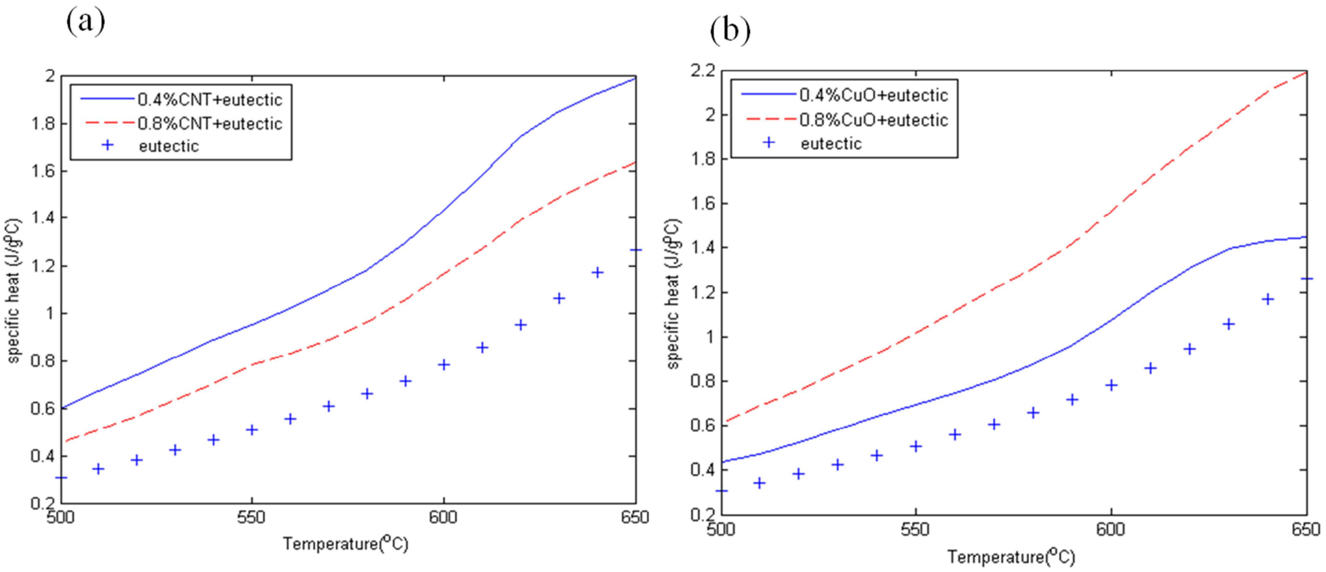


Figure 4. *Variation of specific heat capacity of pure eutectic and nano heat transfer fluid (a) carbon nanotubes (b) copper oxide nanopartilces with temperature.*

5. Conclusion

- The research succeeded in achieving enhanced thermo-physical properties by synthesizing an efficient nano heat transfer fluid by doping base fluid with nano sized particle.
- Designed nanofluid has low melting point, high thermal stability and high specific heat capacity. CNT and CuO are proved to be promising nanomaterial for enhancing these properties.
- It is evident from TGA results that nanofluid is stable till 600°C. It has low melting point i.e 60°C.
- From DSC results it is concluded that enhancement in specific heat capacity is due to addition of selected nano materials. Doping molten salt with CNT and CuO nanoparticles results in enhanced specific heat capacity.
- In conclusion, these results are noteworthy for CSP technology. The increment in these thermo-physical properties can enable to the reduce cost of solar thermal power due to be operative at higher temperatures, hence higher thermodynamic efficiency, lesser material required with higher efficiency, therefore low material cost.

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