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Comparing Synthesis Approach of Two Hybrid Nanoparticles Encapsulating Paraffin Wax

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Abstract: *Many innovative concepts and models are being considered to make Nano fluid technology more and more efficient and cost effective. In this article we have illustrated the synthesis process of hybrid nanoparticles which encapsulate paraffin wax, serving as a suitable heat exchanger when dispersed in a heat transfer medium such as propyl glycol (PG), ethyl glycol (EG), water/ glycol mixture or even fluorocarbons. We have employed two different approaches for the synthesis of two hybrid nanoparticles with an outer-metal shell of copper oxide and silver. We analysed the morphology and structure of the nanoparticles synthesized and concluded that copper oxide nanoparticles synthesized were spherical in structure with a size ranging from 250nm to 550nm, however the silver hybrid nanoparticles synthesized were agglomerated nanostructures, due to high electrostatic attraction between paraffin wax and silver nanoparticles. This study showed that the electrodeposition approach was more efficient in the synthesis of hybrid nanoparticle than the hetero-flocculation approach.*

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I. Introduction

The high technology industries which deal with modern problems of power engineering and nanotechnologies are becoming more and more demanding, attracting ample research interest in order to replace obsolete methods of heat dissipation management. The conventional approach to increase the cooling rate requires an undesirable increase in the size of the thermal management systems, and hence creates the necessity for miniaturization of cooling systems and development of methods for enhanced heat transfer control. The topic of heat transfer intensification has met great challenges, which include enhancing thermal conductivity of a heat carrier [5], increased tolerance to agglomeration[6] and understanding the fluid-particle interface[7,8]. The use of conventional heat transfer fluids such as water, engine oil or ethylene -glycol mixture (EG) greatly impedes the cooling performance of the system. However, nanofluids are believed to be the next generation heat transfer fluids offering higher energy efficiency, low operating costs and better performance. Although many kinds of additives are employed for synthesizing nanofluids, copper nanoparticles have attracted much attention due to their quality of increasing thermal conductivity significantly[2,3,4], reporting up to 23.8% increase at volumetric concentration of 0.1%.[1]Phase change materials (PCM) have an inherent drawback of low thermal conductivity. However, they have been utilised extensively in thermal energy storage systems (TES) during these recent years. The poor thermal performance of PCMs leads to small heat transfer rate, resulting in low efficiency thermal management systems.Based on greater surface to volume ratio, substitution of non-enhanced PCM with encapsulated PCM should provide substantial heat transfer enhancement. Increasing thermal conductivity of PCMs for enhancing thermal performance of the latent heat storage systems is advantageous, providing a feasible, effective and organic system.Saw C. Lin and Hussain H. [14] produced Cu–PCM nanocomposite for TES in a solar collector in order to enhance the thermophysical properties of pure paraffin wax by incorporating of Cu -nanoparticles into it. Likewise, many have reported different methods of enhancing thermal conductivity [11] and thermal performance [12, 13] of the paraffin wax. Furthermore, the nanoparticle properties such as uniformity and stability significantly affect the nanofluid production and their prolonged operating status. The mentioned characteristics divide the existing nanofluid production methods into single-stage and two-stage approach [10].The nanoparticles reported in this article can be employed by two-stage synthesis method of nanofluid, where the first step is to synthesize the nanoparticles and then introduce them into the desired fluid. In comparison, the single-stage method is best suited for metal nanoparticles and the two-stage method is employed for the particles of oxides or metal oxides, because of their high tolerance to agglomeration [9]. The combination of an outer metal-shell provides new functionalities to the nanostructure such as high thermal conductivity and also serves as a robust layer to prevent the leakage of the PCM. Here we report the synthesis of hybrid nanoparticles which encapsulate paraffin wax for the applications of latent heat storage systems. Copper and silver have been chosen to synthesize the outer metal shell of this hybrid nanostructure. This article outlines two different synthesis approach using copper and silver and helps the reader analyse the efficiency and feasibility of the synthesis process.

II. Experimental Implementations

Materials

The paraffin wax pellets (M.P. 56-58 C) used in the present investigation were purchased by LobaChemie, India. The chemicals employed for the synthesis of a outer copper shell were: Sodium Stearate (Sigma Aldrich;Purity 88% fatty acids), Stannous chloride ,palladium chloride , Copper sulphate pentahydrate and Potassium sodium tartaratetetrahydrate. For the synthesis of Silver metal shell, Silver nanoparticles were purchased from Sigma Aldrich (10 nm) and they were used in the form of dispersion. Other substances used to facilitate the experiment were Hydrochloric acid, Sodium Hydroxide, Formaldehyde and ultrapure water.

Synthesis of Silver Hybrid Nanoparticles

Paraffin wax pellets (2% w/w)were heated above there melting point with sodium stearate solution (5mM). The resultant emulsion was allowed to cool below the melting point of PCM, and hence a dispersion of the paraffin was obtained in water. The finely dispersed emulsion was subjected to high shear mixing in order to obtain the paraffin core particles in nanometer range. For this purpose, Planetary ball mill (100PM, Retsch) was used to homogenise the emulsion at 350 rpm.The emulsion obtained was then analysed for its particle size by means of a Nanoparticle size analyser (Brookhaven 90 plus;PSA). The PSA determines the size of nanoparticles by detecting fluctuations in light scattering through the nanoparticle solution. The effective diameter was observed to be 201.4 nm, where the polydispersity of the solution was observed to be 0.283. The polydispersity value indicated that the particles in the emulsion had a narrow distribution and were uniformly dispersed. The dispersion obtained was stable and the formation of outer metal shell was carried out in the next step by hetero-flocculation method.Synthesis of metal shell was done by the hetero-flocculating silver nanoparticles on the surface of the PCM. Electrostatic attraction was established between paraffin particles and the silver nanoparticles with help of a stabilizer Sodium stearic acid.The PCM core particles obtained after shear mixing were suspended in ultrapure water along with the stabilizer in the flask. The atmosphere created inside was the flask was inert by flushing the flask with nitrogen gas. Further, the silver nanoparticles purchased from sigma Aldrich (10nm) were added to the mixture. The synthesised nanoparticles were dried and analysed with microscopy techniques.

Synthesis of Copper-oxide Hybrid Nanoparticles

The uniformly distributed emulsion of paraffin wax and water was obtained by following the same steps as mentioned in 2.2. In order to synthesize a copper shell on the paraffin particles, copper was reduced on the surface of the paraffin particle. In this electrodeposition method, the paraffin emulsion was exposed to a sensitizer solution of Hydrochloric acid (10.9%) and 0.75 gm stannous chloride, maintaining the pH of the mixture at 9. After sensitizing the surface of the parrafin particles the surface was activated by a metal catalyst, here the catalyst used was palladium chloride used in most electroplating techniques. The exposure time determines the thickness of the coating on the paraffin particles. Here, the exposure time was taken as 11 min for the catalyst activation. The next step was to successfully synthesize a copper outer shell on the paraffin particles which was done by reducing the copper sulphate pentahydrate with the help of Formaldehyde (1.12%).The pH was maintained by adding sodium hydroxide into the solution and Potassium sodium tartaratetetrahydrate (0.65gm/90m) was used as a stablizer.

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2$$

The copper ions are deposited on the paraffin particles which form a continuous shell and form a pcm-metal shell. The copper nanoparticles formed a thin oxide layer when exposed to the air. The mixture was further sonicated and diluted for microscopy analysis.

III. Results and Conclusion

The hybrid nanoparticles obtained from both approaches were analysed in terms of morphology and structure. The sample containing copper oxide nanoparticles had a size range varying from 80nm± to 550 nm± and were spherical in shape. The sample purity was appreciable and the concentration of nanoparticles in the sample was very high, thus it was diluted before performing microscopic analysis. The liquid sample of nanoparticle was dried in the oven at 90 °C till a black ash like powderwas obtained for the analysis of elemental composition of the nanoparticles synthesized. The EDAX report confirmed the deposition of the copper oxide on the surface of the paraffin particles.On the other hand,the sample containing silver nanoparticles had a very large size range, making it difficult to make an analysis about the shape and morphology. Many nanoparticles were observed to be extremely small (40 nm±) and many had the size as much as 750nm±. The nanoparticles observed were highly agglomerated to be classified into nanoparticles. The high agglomeration between Silver and paraffin wax was obtained due to the electrostatic interaction between silver nanoparticles and paraffin wax. The concentration of spherical silver nanoparticles with a size range between 250 nm± to 350 nm± was very low. We concluded that electrodeposition method was feasible and effective for synthesizing hybrid nanoparticles encapsulating paraffin wax. These resultant hybrid nanoparticles obtained can be dispersed in a heat transfer medium such as propylene glycol (PG), ethylene glycol (EG) or glycol/water mixtures and fluorocarbons to produce heat transfer nanofluid. This fluid can be used to absorb the waste heat of a system which could be then carried to the sink. The concentration of nanoparticles in the nanofluid can be kept between 2% to 50% by weight in its respective heat transfer fluid. However, the silver-paraffin wax n anoparticles can be employed for the application of thermal energy storage systems and can be used as fillers. Due to the presence of silver nanoparticles, the composite exhibits excellent thermal conductivity and thermal performance.

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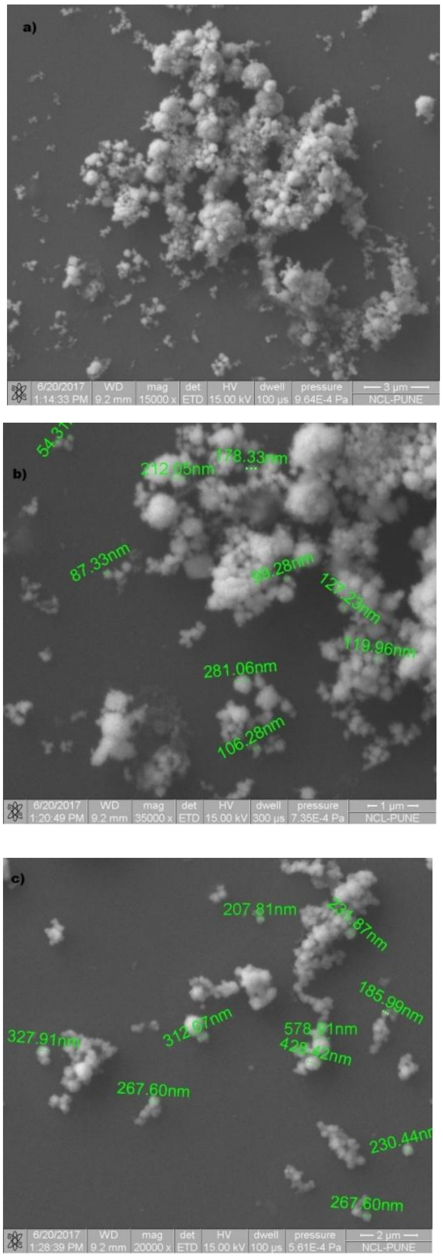
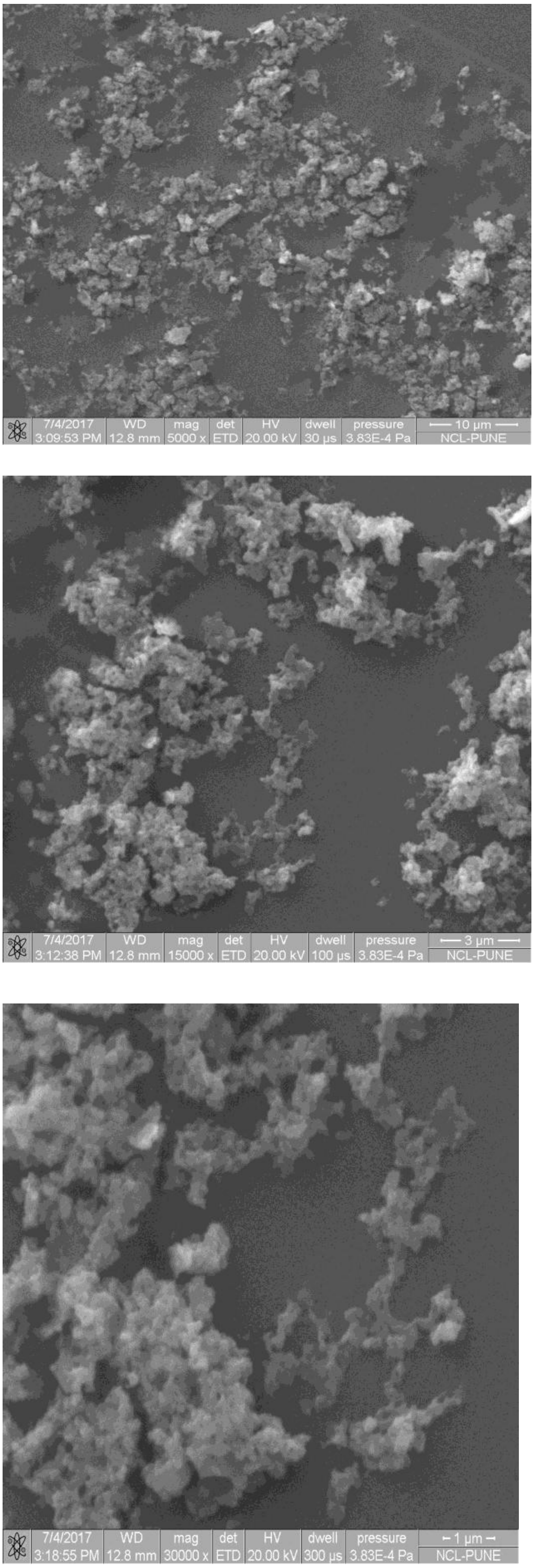
Images and tables

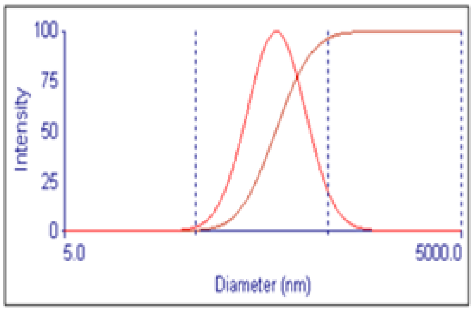


SEM images for Copper-oxide hybrid Nanoparticles encapsulating paraffin wax



SEM images for Silver hybrid nanoparticles.

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	202.0	107.0	0.281	7.5/ 96.21%
2	198.3	104.8	0.279	3.0/100.00%
3	203.5	109.7	0.291	7.5/ 98.88%
Mean	201.2	107.2	0.284	6.0/ 98.36%
Std. Error	1.5	1.4	0.004	1.5/ 1.13
Combined	201.4	107.1	0.283	6.2/ 98.36%



Lognormal Size Distribution

The above table gives the effective diameter as 201.2nm, +/-2nm, where the polydispersity of the solution was observed to be 0.283. This data was obtained from Nanoparticle size analyser (Brookhaven 90 plus; PSA).

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