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ARTICLE TYPE

Ultrafast Thermal Charging of Inorganic Nano-Phase Change Material Composites for Solar Thermal Energy Storage

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- ¹⁰ The present research article reports the heat transfer characteristics of nano-phase change material (NPCM) composites: nanographite (NG)-PCM composites and multi-walled carbon nanotube (CNT)-PCM composites. For the preparation of NPCM composites, inorganic PCM, magnesium nitrate hexahydrate (Mg(NO₃)₂.6H₂O) was used as the pristine PCM and nanocellulose was used as a stabilizing agent. NG-PCM composites were prepared by varying the concentration of NG from 0.1- 0.6 wt %,
- ¹⁵ whereas CNT-PCM composites were prepared using 0.1 and 0.2 wt% of CNT. The prepared NPCM composites exhibited enhanced thermal conductivity and a faster heating rate than pristine PCMs. Two different experimental setups were used for investigating the heat transfer characteristics of prepared NPCM composites during the melting and solidification processes: (i) conventional heating and (ii) solar illumination. The experimental observations indicated a higher heat transfer rate in NPCM composites as
- ²⁰ compared to pristine PCM for both experimental setups. It was observed that the heating melting and solidification rate using conventional heating setup increased by 48% and 77%, respectively, for NG-PCM composites (at 0.6 wt %) & 24% and 15 %, respectively for CNT-PCM composites (at 0.2 wt %). Upon solar illumination, both NG-PCM and CNT- PCM composites demonstrated an ultrafast heating rate (of the order of few seconds) and a higher heating temperature than the conventional heating based
- ²⁵ approach. The ultrafast heating of NPCM composites upon solar illumination was attributed to the plasmonic heating effect of carbon nanomaterials, which instantly convert optical energy into heat at nanometer scale in addition to conventional thermal diffusion based slow heating, the sole mechanism responsible for slow heating of PCM composites in conventional heating setup. Out of the two carbon nanofillers used, CNTs were shown to have better heat transfer performance than NGs to collect, convert ³⁰ and store the broad spectrum solar energy as thermal energy.

1 Introduction

World-wide, there is an intense research going on to harness renewable energy sources with special emphasis on solar energy, as it is abundant, clean and fairly available to all. Sustainable ³⁵ utilization of the solar energy can be done with thermal energy storage systems using phase abange metarials (PCMs) a special

- storage systems using phase change materials (PCMs), a special class of materials having a large heat of fusion and a sharp melting point¹. Thermal energy storage (TES) using PCMs provides an elegant and realistic solution to increase the
- ⁴⁰ efficiency of the storage and use of energy in many domestic and industrial sectors^{2, 3}. Importantly, the application of PCMs for energy storage can reduce the mismatch between supply and demand, improve the performance and reliability of energy systems and can play an important role in conserving energy.
- ⁴⁵ TES may involve only sensible heat storage, latent heat storage or a combination of both. TES system based on latent heat is the

most popular technique due to its salient features like high storage density for given volume and storing thermal energy under isothermal conditions⁴. A typical latent heat storage system ⁵⁰ based on PCMs has three important functions: charging, storing and discharging. PCMs are broadly classified into two groups: organic (paraffins and non-paraffins) and inorganic (salt hydrates and metallics). Depending on the characteristics of high latent heat, high specific heat and high thermal conductivity, both ⁵⁵ organic and inorganic PCMs have played an important role in various fields extensively^{5, 6}.

In recent decades, inorganic PCMs such as salt hydrates and their mixtures have been investigated for thermal energy storage. Due to their better thermal properties, inorganic salt hydrates ⁶⁰ have been used as direct heat transfer medium in industrial applications. Particularly, various nitrate based salt hydrates and their composites have attracted tremendous research interest due to their high value of thermal conductivity and high volumetric latent heat storage capacity as compared to organic PCMs such as paraffins^{7, 8}. Recently, researches have focused on improving the thermal properties of heat transfer and energy storage medium. As far as thermal conductivity enhancement of PCMs is ⁵ concerned, nanomaterials such as metallic/oxide nanoparticles, single and multiwalled carbon nanotubes (CNTs) and the graphene/graphite nanoplatelets (GNPs) have been proposed⁹⁻¹².

- Among the various nanomaterials examined, carbon nanomaterials have been preferred because they possess 10 extremely high thermal conductivity and relatively low density. Although the effects of adding a variety of carbon nanomaterials on the thermal conductivity and energy storage properties of
- nano-PCM (NPCM) composites have been investigated extensively in the literature¹³⁻¹⁵, the problem of forming stable ¹⁵ NPCM composites has not been dealt. The innovation of our current research work suggests the incorporation of stabilizing agent, in the form of nanocellulose, mixed together with carbon
- nanomaterials and inorganic PCM to produce stable NPCM composites. In the present research article, we demonstrate a ²⁰ rapid heat transfer rate in NPCM composites using two different carbon nanomaterials, nanographite (NG) powder and multi-walled carbon nanotubes (CNTs), as compared to pristine PCM using conventional heating and illumination with sunlight. Under solar illumination condition, a much higher heating rate and
- ²⁵ temperature was obtained than the conventional heating approach. The highly accelerated heating rate of NPCM composites upon solar illumination was attributed to the plasmonic heat generated by well-dispersed carbon nanomaterials. We corroborate our studies by carrying out control
- ³⁰ experiments using water mixed with NGs or CNTs, which showed rapid generation of steam in open air under solar illumination.

2 Experimental Section

35 2.1 Materials and sample preparation

An inorganic salt hydrate, magnesium nitrate hexahydrate $(Mg(NO_3)_2.6H_2O)$, with a melting point of 90 °C was adopted as the pristine PCM, while commercially-available nanographite ⁴⁰ (NG) powder, with an average particle size of 100-200 nm, and

- CNTs, with an average length and diameter of 1-10 µm and 20-50 nm, respectively, were procured from Reinste, Germany. The NG-PCM composites were prepared following a melt-mixing scheme, which consisted of two steps. In the first dispersion step,
- ⁴⁵ NGs were added to the molten salt hydrate with variable concentrations, and the suspensions were then prepared by strong shear mixing with a magnetic stirrer for 15 min, followed by an intensive ultrasonication for 45 min. To the above solution, nanocellulose (synthesis method of nanocellulose is described
- ⁵⁰ below) was mixed and thoroughly stirred. The nanocellulose used above acts as a stabilizing or nucleating agent, which helps in preventing the problem of phase segregation and supercooling, an inherent problem encountered in salt hydrates¹⁶, when they undergo several cycles of melting and freezing. In the second
- ⁵⁵ step, the suspensions were poured into a mold, and were then allowed to solidify at ambient temperature (~25 °C) to form solid composite samples. Complete solidification of the samples took about 1 h. Different NG-based PCM composites were prepared,

with mass fractions of NGs ranging from 0.1 wt% to 0.6 wt%.

⁶⁰ CNT-PCM composites, with 0.1 wt% and 0.2 wt% of CNTs, were obtained according to the above-described procedure; except for a minor modification in the first step that instead of adding CNTs directly to the molten salt hydrate, CNTs were first dispersed in SDS (sodium dodecyl sulphate) surfactant solution ⁶⁵ and then added to molten salt hydrate. This is due to the insolubility of CNTs in water and hence CNTs do not get dispersed in salt hydrate. The preparation of CNT/SDS solution is described later in this section.

Synthesis of Nanocellulose: Nanocellulose was prepared ⁷⁰ following a methodology involving acid hydrolysis of cellulose¹⁷. Typically, cellulose powder (10 g) was soaked in a 100 ml NaOH solution (0.5 M) for 2 h followed by rinsing with distilled water. Bleaching treatment was then carried out with a 100 ml 0.5 M sodium chlorite solution (pH 4) for 2 h at 50°C followed by ⁷⁵ rinsing with distilled water. The pre-treated cellulose was then acid hydrolyzed (made of 40 ml distilled water + 20ml of 12.1 N HCl + 40 ml of 36 N H₂SO₄) with continuous stirring for 3h at 70°C and then repeatedly rinsed with distilled water for several times. The resulting nanocellulose sample was then sonicated at ⁸⁰ 80°C for 3h. Nanocellulose sediment, thus obtained, was washed with distilled water and 5% Na₂CO₃ repeatedly to attain a pH ~ 7. The final working solution of nanocellulose was prepared by

sediment.
⁸⁵ Preparation of CNT/SDS solution: To 10 ml of water, 1 g of sodium dodecyl sulphate (SDS) surfactant powder was added and mixed thoroughly to obtain a clear SDS solution. To this solution, 20 mg of CNT was added, mixed well and ultrasonicated for 3-5 minutes to obtain well-dispersed CNT/SDS solution.

adding 100 ml of distilled water to the above neutralized cellulose

2.2 Characterization Techniques

The morphology of NGs and CNTs were observed using scanning electron microscope (SEM, Zeiss EVO-18). In addition, ⁹⁵ morphologies of NGs and CNTs were also inspected to examine the dispersion of the nanomaterials in the respective NPCM composites. The effective thermal conductivity of solid NPCM samples was also measured using a Linseis Transient Hot Bridge -Thermal Conductivity Meter (THB6N43) at ambient ¹⁰⁰ temperature.

2.3 Experimental setup and procedure

Following two experiments were conducted to explore the ¹⁰⁵ heating rate of pristine PCM and NPCM composites: (i) conventional heating and (ii) solar illumination.

Experimental setup of the conventional heating system: In order to investigate the transient heat transfer during melting and solidification of NPCM composites, an experimental setup ¹¹⁰ featuring a heated-from-below configuration was designed as shown in figure 1. The set-up consisted of a hot plate, having a set temperature range of 30-400°C and an attached temperature sensor. A test cell (glass vial) containing pristine PCM or NPCM, with a thick thermal insulation layer, was kept on top of the hot

¹¹⁵ plate. The amount of the PCM material filled in the glass vial was 10g. The PCM (or NPCM) temperature in the conventional

heating experimental setup was measured by inserting the attached temperature sensor into the PCM by drilling a small hole on the lid of vial, as shown in fig. 1. The temperature readings were recorded by a digital thermometer connected directly to s temperature sensor.

For melting processes, the temperature of NPCM composites was increased at rate of 5°C/min. For solidification experiments, the test cell containing molten PCM or NPCM composites was made to undergo natural cooling process. In this way, melting and

- ¹⁰ solidification processes for the pristine PCM and NPCM composites were repeated for assessing their phase change temperatures. It should be mentioned that the first few melting/resolidification cycles were carried out to eliminate the effect of uneven heating on the specimens.
- ¹⁵ To see the efficacy of PCM as suitable solar thermal energy storage, we carried out heat transfer studies under direct solar illumination, whose details are as follows.

Solar illumination and solar water heating experimental setups: The schematic diagram of solar illumination experimental set up

- ²⁰ used for analyzing the melting and solidification characteristics of PCM and NPCM composites under direct solar irradiation is shown in fig. 2. The experimental setup consists of a 0.3- m² Fresnel lens (30 cm focal length), used to focus sunlight into a 20 mL beaker containing NPCM composites, which was in turn
- ²⁵ placed in an insulated tank. The temperature of NPCM composites was measured using a k-type thermocouple (TC) and recorded at regular intervals of time. A solar water heating experimental set-up (fig. 3) was used to study the evolution of steam generation in which a beaker containing NPCM composites
- ³⁰ was kept inside a water-filled beaker and a k-type TC was used to monitor the temperature of water. The amount of water to be heated in the vessel was 60 ml. It has to be mentioned that both the solar illumination and solar water heating experiments were carried out outdoor under natural sunlight irradiation, whose
- ³⁵ intensity was measured using a pyranometer (Hukseflux USA, model SR11 first class pyranometer) and found to be 550 W/m².

3 Results and Discussion

40 3.1 Characterization of PCM and NPCM composites

The SEM image of the pristine carbon nanomaterials, CNT and NG, used as nanofillers in our experiments, are shown in fig. 4a and fig. 5a, respectively, which reveal a size distribution as ⁴⁵ reported by the supplier. The SEM image of pristine PCM (Mg(NO₃)₂.6H₂O) is shown in fig. 4b, which looked like a milky

- substance. It is clearly seen from the SEM image of CNT-PCM composites (fig. 4c) that CNTs were well dispersed in the pristine PCM. The SEM image at higher magnification (fig. 4d) indicates
- ⁵⁰ that the CNTs were well dispersed in the PCM with the large agglomerates of the raw CNTs being broken into much smaller clusters during sample preparation. The SEM image of NG-PCM composites, shown in fig. 5b, reveals that the NG-PCM composite is more tightly packed compared to the NGs alone (fig.
- 55 5a) because the layers of NG in NG-PCM composites are completely dispersed in salt hydrate.

In order to study the effect of the addition of carbon nanofillers (CNT and NG) in the enhancement of thermal conductivity of PCM, we performed the thermal conductivity measurements on ⁶⁰ NPCM composites by varying the nanofiller concentration. Thermal conductivity of pristine PCM (pure salt hydrate) was measured and found to be 0.58 W/(mK). On addition of 0.3 wt. % of NGs, the thermal conductivity of the NPCM composite increased to 1.13 W/(mK). The increase in the thermal ⁶⁵ conductivity of PCM with the increase in the concentration of NGs (0, 0.3 wt% and 0.5 wt%) is presented in Table 1. Overall, with a small NG addition of 0.5 wt%, a strikingly high, 271 % enhancement in thermal conductivity was achieved. Two main reasons which could be attributed to the enhancement in the ⁷⁰ thermal conductivity (*k*) of NPCM composites are: (i) the presence of highly conductive carbon nanomaterials, graphite¹⁸ having *k* ~ (200-500) W/(mK) and CNTs¹⁸ having *k* ~ (2500-3000) W/(mK) and (ii) uniform dispersion of nanofillers into the

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molten salt.

3.2 Experimental results using conventional heating experimental set up

The enhancement of the thermal transfer rate was investigated by 80 comparing the melting and solidification processes of PCM and NPCM composites using conventional heating approach. Heat transfer experiments were performed with the pristine PCM followed by NPCM composites (NG-PCM and CNT-PCM composites). Figure 6 represents the melting curves of the pristine 85 PCM and NG-PCM composites with different concentrations (0.1-0.6 wt. %) of NGs. As shown in Fig. 6, pristine PCM and NG-PCM composites were at ambient temperature at the beginning of melting process. The temperature of the pristine PCM and NG-PCM composites gradually increased until it ⁹⁰ reached their respective phase transition temperature (~ 90°C). It was observed that pristine PCM started to melt at approximately 50 minutes from the starting point. As the concentration of NG was increased from 0.1 to 0.6 wt. %, a drastic decrease in the melting time of NG-PCM composites was achieved. At the ⁹⁵ highest concentration of NG used (0.6 wt %), the melting time of NG-PCM composite was only 26 min. This represents an overall reduction of 48 % in the melting time of the NG-PCM composite at 0.6 wt% compared to that of pristine PCM. Further, the solidification curves of the pristine PCM and NG-PCM 100 composites were investigated. At the start of solidification process, temperatures of pristine PCM and NG-PCM composites were found to be 107°C. As the natural cooling occurred, temperatures of the pristine PCM and NG-PCM composites decreased and it continued until their respective solidification ¹⁰⁵ point. The solidification curves of figure 7 showed a similar trend as those of melting curves, i.e. the solidification time decreased as the concentration of NG was increased from 0.1 to 0.6 wt%. It was observed that the solidification time of the NG-PCM composite at 0.6 wt% was reduced by 77% compared to that of 110 pristine PCM. The above results confirm that our NG-PCM composites exhibit a high heat transfer rate, which improves the energy utilization efficiency during heat charging and discharging processes.

Further, melting and solidification experiments were ¹¹⁵ conducted on CNT-PCM composites, using the conventional heating experimental setup, at 0.1 and 0.2 wt % concentrations of CNTs. The temperature profiles of CNT-PCM composites, shown 75

in fig. 8 and fig. 9, showed a similar trend as those of NG-PCM composites, i.e. the rate of melting/solidification in CNT-PCM composites increased as the concentration of CNTs increased.

- An overall reduction of 24% and 15% in the melting time and s solidification time, respectively, of the CNT-PCM composite at 0.2 wt% was achieved compared to that of pristine PCM. It was observed that the solidification time of the NG-PCM composite at 0.6 wt% was reduced by 77% compared to that of pristine PCM.
- These results clearly indicate the significant effect of carbon ¹⁰ nanomaterials (NGs and CNTs) in enhancing the thermal conductivity and heat transfer characteristics of the NPCM composites. The observed results of rapid heating and cooling of nano-PCM composites (CNT-PCM and NG-PCM composites) is mainly attributed to the high thermal conductivity of the network
- ¹⁵ of carbon nanofillers (CNTs and NGs) that provide a path of lower resistance for phonons to travel. In addition, the aspect ratio and interfacial contact area of carbon nanofillers as well as strong interface between carbon nanofillers and the PCM also help to increase the heat transfer rate of carbon-PCM
- ²⁰ nanocomposites¹⁹. It has been reported that since the dominant heat transfer mechanism is due to the lattice vibrations or phonons; poor phonon coupling in the vibrational modes at the PCM-nanofiller and filler-filler interfaces cause thermal resistance, also called the Kapitza resistance, which decreases the ²⁵ overall thermal conductivity of the material²⁰ and hence the

heating and cooling rate of nano-PCM composites.

It is true that dispersed nanoparticles increases the thermal conductivity of PCM with a reduction in the solidification or melting time of NPCM composites. However, thermal

- ³⁰ conductivity is actually not the sole parameter that affects the rate of temperature variation in NPCM composites. Accompanying with the increased thermal conductivity, the presence of the nanoparticles could also increase the viscosity of NPCM composites as a penalty, leading to degradation of natural
- ³⁵ convection and hence the decrease in the melting rate. Melting of NPCM composites has been shown experimentally to be either enhanced or deteriorated, depending on the relative intensity of the two competing effects: i.e., enhanced heat conduction and weakened natural convection. Hence, it is required to justify an
- ⁴⁰ optimum concentration of nanoparticles that should be dispersed in PCM to enhance the thermal conductivity of the composite with minimizing the negative impacts of other properties like viscosity. From several published literature on NPCM it is clear that the latent heat capacity of PCM decreases with increasing
- ⁴⁵ nanoparticle concentration although it could increase in special cases. Different properties of nanoparticles such as variation in size and modification in surface properties affect the degradation of latent heat capacity in different ways. As with the case of viscosity, one has to determine an optimum nanoparticle
- ⁵⁰ concentration for which thermal conductivity enhancement is maximum and latent heat capacity degradation is minimum, which would result in better heat transfer characteristics of the NPCM composites.

The heating process in conventional heating approach proceeds ⁵⁵ via conventional thermal diffusion, which relies on the slow thermal heating from the hot zone, where the heat is absorbed, to the rest part of thermal storage media (PCM). It is to be noted that the phase change temperatures of PCM nanocomposites show variation with respect to the fraction of nanomaterials, ⁶⁰ particularly in the case of NG-PCM composites. The result may be attributed to the introduction of nanographite layers into the pristine PCM, which affected the phase change process²¹. Our results on phase change temperatures are in fairly good agreement with those reported by F. Salaün et al.²² who reported ⁶⁵ that the phase change of polymer nanoparticles based PCM (paraffin) occurs on a wider temperature interval. They attributed their result to the ordered structure of paraffin molecules around the polymer nanoparticles. To perform a more real-time analysis of the heating and cooling phenomena and to check any ⁷⁰ possibility of further reduction in melting time of NPCM composites, we performed another set of melting experiments under solar illumination (described below in detail).

3.3 Solar irradiation experimental results

The experimental setup for the solar illumination experiment is shown in fig. 2. The solar irradiation experiments were conducted to compare the rate of charging (melting) of NPCM composites (NG-PCM and CNT-PCM) with pristine PCM. Our experimental ⁸⁰ observations clearly indicated drastic reduction in melting time of NPCM composites as compared to that of the pristine PCM, a much higher reduction in melting time as compared to that obtained in conventional heating approach. It was observed that the time taken to completely melt pristine PCM was 45 min, (see ⁸⁵ Table 2), the melting time of NPCM composites (0.1 wt %) drastically reduced to few minutes, i.e. 1 min for NG-PCM composites and 30 sec for CNT-PCM composites.

Our experimental observations of drastic reduction of melting time of NPCM composites under solar illumination could be ⁹⁰ attributed to the combined effect of plasmonic heating of uniformly dispersed carbon nanomaterials and the conventional thermal diffusion based approach. Upon solar illumination, NPCM composites absorb solar energy, converting it into thermal energy via plasmonic heating of uniformly dispersed carbon ⁹⁵ nanofillers. The resultant thermal energy is stored in NPCM composites, during the phase transition of the composites. It was observed that, even at a low concentration of 0.05 wt. % of nanomaterials used (NGs or CNTs), the time taken to melt NPCM composites was same as that obtained for 0.1 wt%.

It is known that the CNTs exhibit absorbance characteristics in 100 the UV-Vis-NIR region²³ as a result of van Hove transitions^{24, 25} which are very important for the effective light harvesting of solar irradiation. CNTs display optical absorptions due to resonant band-to-band transitions 25. Upon solar irradiation, the 105 solar incident energy drives mobile carriers (free electrons) inside the CNTs to oscillate at its resonant frequency (plasmonic oscillations) and the energy gained by carriers turns into heat^{26, 27}. This is known as the plasmonic heating effect. The localized heat thus generated then diffuses away from the nanomaterial due to 110 thermal diffusion and leads to an elevated temperature of the surrounding medium. In our experiment, upon solar irradiation, the temperature of the CNT-PCM composites rapidly increased as compared to the pure salt hydrate, which is ascribed to the plasmonic heating of CNTs because CNTs function as an 115 effective photon captor and molecular heater. Simultaneously, the temperature of the control sample (pristine PCM) also gradually

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increased because the salt hydrate absorbed the near-infrared light of the solar irradiation. Similarly, graphite nanostructures absorb light more efficiently for wavelengths in the visible and near-IR part of the spectrum²⁸. The optical properties for wavelengths s longer than ~200 nm are believed to derive predominantly from transitions within or between the π -bands²⁹.

Thus, the solar illumination experiments on NPCM composites illustrate that the phase transition of the composites occurs upon solar irradiation, when the composites absorb solar radiation,

¹⁰ converting the radiation into thermal energy due to plasmonic heating and storing the resulting thermal energy in PCMs. These NPCM composites with high thermal conductivity can shorten the time of heat storage and release, which improves the energy utilization efficiency. In order to demonstrate a real-time ¹⁵ application using NPCM composites, we carried out solar water

heating studies as described below.

3.4. Solar water heating using NPCM composites

- ²⁰ The experimental setup for solar water heating is shown in fig. 3. Solar water heating experiments were conducted using glass and aluminium beakers. Our experimental observations, shown in fig. 10, indicate that when pristine PCM (salt hydrate) was used, the temperature of water (in glass beaker) remained around 60°C
- ²⁵ (curve 1 of fig. 10) after 30 minutes. When NG-PCM composite was used, the water temperature reached 60 ° C in just 6 min (curve 2 of fig. 10). This could be attributed to the rapid solar thermal melting of NG-PCM composites as compared to pristine PCM via plasmonic heating and thermal diffusion, as described
- ³⁰ before. In order to provide an enhancement in the heat transferred from NPCM composites to water, we slightly modified our setup by replacing glass beaker with an aluminium beaker, which acts as a suitable heat exchange surface between NPCM composites and water. Under this condition (curve 3 of fig. 10), the system
- ³⁵ reached high temperature quickly within 2-3 mins, along with generation of steam. There are few available literatures reporting steam generation using carbon and metal nanoparticles upon solar irradiation³⁰⁻³². Using absorptive nanomaterials (metal and carbon) dispersed in water, Halas *et.al.*³¹ demonstrated an ⁴⁰ efficient direct steam generation upon solar illumination. Chen
- ⁴⁰ efficient direct steam generation upon solar multimation. Chen et.al.³² reported development of an approach and corresponding material structure for solar steam generation while maintaining low optical concentration and keeping the bulk liquid at low temperature with no vacuum. Our experimental results clearly
- ⁴⁵ show that the high thermal conductivity of carbon nanomaterials together with UV-Vis sunlight-harvesting property and high light-to-heat conversion has led to enhancement in thermal conductivity of NPCM composites and thus better heat transfer performance of these composites. Simultaneously, the generated
- ⁵⁰ thermal energy is stored in the NPCM composites with a high energy storage density, which could be used for different applications like air heating. These experiments clearly show the broad-spectrum application of PCM nanocomposite for solar thermal collection, conversion and storage applications. With
- 55 these results, the newly prepared stable NG-PCMs and CNT-PCM composites could be considered to be efficient PCMs for thermal energy storage and solar water/ air heating system due to its enhanced heat transfer characteristics and good thermal

stability.

60 Conclusions

Stable salt hydrate-based nano-PCM (NPCM) composites have been prepared using carbon nanomaterials (NG and CNT) as nanofillers and nanocellulose as stabilizing agent. NG-PCM composites were prepared by varying the concentrations of NG 65 from 0.1-0.6 wt %, whereas CNT-PCM composites were prepared with 0.1 and 0.2 wt% of CNT. The prepared NPCM composites (NG-PCM and CNT-PCM composites) exhibited remarkable sunlight-harvesting, high light-thermal conversion efficiency with enhanced thermal conductivity. Both NPCM 70 composites have been used to demonstrate the fast and uniform heating as compared to pristine PCM using conventional heating approach as well as incident solar energy. Upon solar illumination, the NPCM composites demonstrated an ultrafast heating rate (of the order of few seconds) and a higher heating 75 temperature than the conventional heating based approach. While the conventional heating approach took 45 min to completely melt NPCM composites, under solar illumination, the melting time of NPCM composites drastically reduced to 1 min for NG-PCM composites and 30 sec for CNT-PCM composites. The 80 ultrafast and uniform heating of NPCM composites upon solar illumination has been attributed to instant optical charging via plasmonic heating of carbon nanomaterials (CNT and NG) in addition to conventional thermal diffusion, which relies on the slow thermal heating from the hot zone, to the rest part of thermal 85 storage media (PCM). It was also found that CNTs have shown better performance than NGs to collect, convert and store the broad spectrum solar energy as thermal energy. Use of these

broad spectrum solar energy as thermal energy. Use of these novel PCM-nano composites will provide alternative, environmental friendly and low cost solution to the current 90 energy demands.

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Fig. 1 Conventional heating system experimental setup.



Fig. 2 Solar illumination experimental setup.



Fig. 3 Solar water heating experimental setup.



Fig. 4 SEM images of (a) CNT, (b) pristine PCM, Mg (NO₃)₂.6H₂O, (c) CNT-PCM composites at low magnification and (d) at high magnification.

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Fig. 5 SEM images of (a) Nanographite (NG) and (b) NG-PCM composites.



Fig. 7 Solidification curves of pristine PCM and NG-PCM composites at different concentrations (wt. %) of NG.



Fig. 8 Melting curves of pristine PCM and CNT-PCM composites at different concentrations (wt. %) of CNTs.



Fig. 6 Melting curves of pristine PCM and NG-PCM composites at different concentrations (wt. %) of NG.



Fig. 9 Solidification curves of pristine PCM and CNT-PCM composites at different concentrations (wt %) of CNTs.



Fig. 10 Variation of temperature of water with time using solar water heating experimental setup.

5 Table 1. Thermal conductivity coefficient of pristine PCM and NG-PCM composites at different mass concentrations (wt. %) of NG.

S. No.	NG (wt.%)	Thermal conductivity coefficient W/(mK)
1	0	0.583
2	0.3	1.138
3	0.5	2.165

 Table 2. Direct solar irradiation experiments conducted on pristine PCM

 and different NPCM composites.

S. No.	PCM or NPCM composites	Time taken to melt PCM
1	Mg(NO) .6H O (Pristine PCM) $_{32}^{32}$ (Pristine PCM)	45 min
2	Mg(NO) .6H O + 0.1 wt.% NGs ${}_{32}$ 2	1 min
3	Mg(NO) $_{32}$.6H O + 0.1 wt.% CNTs	30 sec

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Text: Ultrafast charging of NG-PCM and CNT-PCM nanocomposites has been demonstrated using conventional heating approach and direct solar illumination experimental setups.





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