Simultaneous solar-thermal energy harvesting and storage via shape stabilized salt hydrate phase change material

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HIGHLIGHTS

• The facile route was introduced to synthesize novel salt hydrate based shape-stabilized PCMs.
• A high enthalpy of fusion (248.3 J/g) with low supercooling degree of 0.1 °C was achieved.
• The thermal conductivity was enhanced up to 114%.
• These novel SSPCMs have shown great thermal cycling reliability and high photo-thermal efficiency of 92.6%.

GRAPHICAL ABSTRACT

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ABSTRACT

The intermittent nature of solar radiation for solar driven applications providing the vast opportunity for phase change materials (PCMs) to reduce the gap between supply and demand of energy. Nevertheless, the widespread utilization of PCMs is limited due to the flow of liquid PCMs during melting, phase separation, supercooling and low heat transfer rate. The ongoing progression of research in this field reveals that there is a high demand for shape stabilized PCMs (SSPCMs) with high energy storage capacity and fast charging and discharging rates. Here, we demonstrated the facile route to synthesize novel salt hydrate based SSPCMs via incorporation of the functionalized graphene nanoplatelets (GNPs). The hydrophilic GNPs not only prevented the PCM leakage but also improved the thermal conductivity and proffered the low supercooling degree. The resultant SSPCMs exhibited a high transition enthalpy (248.3 J/g) with low supercooling degree of 0.1 °C. The addition of graphene nanosheets significantly enhanced the solar absorption characteristics of pure PCM and simultaneously offered the high photo-thermal efficiency of 92.6%. This strategy concurrently enhanced the thermal conductivity of pure salt by 114% that accelerates solar-thermal energy storage rates while maintaining the high energy storage capacity. These novel SSPCMs have shown great thermal cycling reliability make them very promising materials for solar-to-thermal conversion and storage.

1. Introduction

Energy crisis and environmental concerns raised as an urgent problems following the enlargement of human society. Given that, exploring renewable energy resources and enhancing the utilization efficiency of traditional energy systems have been proposed to overcome
this challenge [1]. The solar energy harvesting and exploitation as distinguished renewable energy resource is a major area for research and development (R&D) [2]. The solar energy harvesting can be done by different energy conversion systems into electricity, heat, or fuel [3]. Even though the costs of solar panels for electricity production have reduced swiftly, technology gaps still exist including low conversion efficiencies less than 50% and high cost of storage technologies [4]. Besides, the majority of the solar energy is delivered when the sun is shining brightly showing that intermittency can be counted as the major criticisms of this energy source. The solar-thermal conversion is another superb approach for utilization of solar energy, in which the solar energy can be harvested and stored in heat storage materials as thermal energy. The conversion efficiency of solar to thermal energy can reach as high as 80% proving that this approach tends to be a promising direction for the future development of solar energy utilization [5,6]. The Key goals for R&D are development of materials that can absorb and convert sunlight efficiently by having great absorption capabilities as well as high energy storage density.

The Phase change materials (PCMs) are playing an important role for solar-thermal applications due to their remarkable potency of storing and releasing large amounts of latent heat at relatively constant temperatures in the phase change process [7,8]. Among various types of PCMs (organic, inorganic, and bio-based), organic PCMs have gained much attention in this research field due to their acceptable thermal energy storage density, wide temperature working range, long term stability, noncorrosive and low toxicity properties [9,10]. However, the commonly occurring issues of organic PCMs used in solar-thermal conversions are their intrinsic low thermal conductivity, fire safety, and high cost [11,12]. The inorganic salt hydrates have shown some major advantages of larger phase change enthalpy, non-flammability, cost effectiveness and so on, offering wide expectation for use in thermal energy storage(TES) applications. Nevertheless, these salts typically suffer from drastic supercooling, phase segregation and corrosivity issues. So, it is necessary to resolve the issues related to supercooling, phase segregation and corrosivity of the inorganic PCMs [13].

Sodium acetate trihydrate (CH₃COONa·3H₂O), a non-toxic crystalline hydrated salt as an inorganic PCM has drawn lots of attention from engineers and researchers around the world, especially during the past decade owing to its suitable melting temperature (around 58.4°C) and large heat of fusion (264 J/g) [14]. Sodium acetate trihydrate (SAT) has been proven to be a promising inorganic PCM candidate in TES applications because of its high energy density and low cost. Unlike organic PCMs, SAT has shown that a high degree of supercooling leads to extra energy release in the beginning stage of supercooling. As a result, less energy is available for the subsequent phase transition or crystallization. Moreover, incongruous melting and phase separation of SAT upon cycling hinder its application for energy storage purposes [15].

In previous studies, several nucleating, thickening and phase transition thermo regulating agents were chosen and combined with SAT matrix to prevail over the aforesaid obstacles to some extent. Song et al. investigated the effect of various nano materials such as AlN, Si₃N₄, ZrB₂, SiO₂, BC₄, and SiB₆ as nucleating agents for SAT. The results showed that the supercooling degree of the SAT can be suppressed by introducing 2 wt% SiO₂, 5 wt% AlN, 4 wt% Si₃N₄ and 10 wt% ZrB₂. The size distribution of nanoparticles has played a key role on supercooling elimination of SAT by considering size ranging from tens of nanometers to about 300 nm [16]. Garay et al. considered Ag nanoparticles (AgNPs) as nucleating agent for polymer/SAT composites. The carboxymethyl cellulose (CMC) was used as thickening agent in this study. The CMC is very well known due to its functionality as a thickener, stabilizer, suspending and gelling agent. It has been extensively considered in many studies as a thickening agent to omit phase separation of SAT during the cycling process [17–19]. Cui et al. reported that a combination of CMC as gelling agent and Cu nanoparticles had stable performance and enhanced the supercooling characteristics and heat transfer of SAT [19]. Also, many other studies reported that some inorganic salts including Na₃HPO₄·12H₂O (DSP), Na₂HPO₄, Na₃HPO₄·10H₂O (TSPP) as well as some organic compounds such as chitin nanowhiskers (CNW) and gelatin can be used as nucleating agents [20–23]. The major outcomes of these studies including the effect of different nucleating and thickening agents on supercooling behavior and energy storage capability of SAT are summarized in Table 1. Despite the fact that these reported methods could achieve relatively acceptable phase change behaviors and good energy density, they have shown some limitations such as poor cyclic stability, degradation and leakage issues as well as low thermal conductivity due to the addition of thickening agents.

As a credible alternative to solve these problems, the shape stabilization including impregnating of salt hydrates into porous materials, such as expanded graphite (EG), vermiculite and expanded perlite has been highlighted due to its simplicity, high efficiency and low price. Deng et al. used vermiculite as supporting material to enhance the supercooling suppression and heat transfer properties of the Na₃HPO₄·12H₂O PCM [26]. In another study, Gu et al. impregnated the SAT into a porous network of EG that provided the form-stable SAT/EG composite with SAT mass fraction of 95% [27]. Most of these studies showed that carbon based materials have a vast potential to be incorporated with inorganic PCMs to improve their thermal conductivity as well as shape stability. Moreover, carbon based materials have a remarkable capability of solar light capture that is always the predominant requirement for solar-thermal energy conversions. In other words, composite PCM materials should not only play a role in thermal energy storage, but also serve as photon capture and heater under the solar radiation [28]. Between the various carbon materials, expanded graphite [29,30], graphene [31], graphene oxide [32–34], carbon nanotube [35], and carbon fiber [36] have been exploited for composite PCMs due to their thermal conduction characteristics and chemical compatibilities. In our previous works, graphene nanoplatelets (GNPs) with different specific surface area have been used as supporting materials for shape stabilization and thermal conductivity enhancement of organic PCMs. The prepared shape stabilized PCMs(SPCPCMs) have shown great shape stability, energy storage density and thermal conductivity [37]. The drastically different features between thermal and physical properties of GNPs and above-mentioned supporting materials are quite intriguing and can shed light on the important mechanisms to

\[\text{Table 1} \]

<table>
<thead>
<tr>
<th>Nucleating agent</th>
<th>Thickening agent</th>
<th>Fraction</th>
<th>Major result of the study</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>CMC</td>
<td>1 wt% Al₂O₃</td>
<td>Latent heat of fusion:232.29 J/g Supercooling degree: 2.3°C</td>
<td>[17]</td>
</tr>
<tr>
<td>AgNPs</td>
<td>CMC</td>
<td>0.6wt% AgNPs</td>
<td>Latent heat of fusion:222 J/g Supercooling degree: 4.69°C</td>
<td>[18]</td>
</tr>
<tr>
<td>Cu</td>
<td>CMC</td>
<td>0.5wt% Cu</td>
<td>Latent heat of fusion:231.4 J/g Supercooling degree: 1.2°C</td>
<td>[19]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>None</td>
<td>1wt% SiO₂</td>
<td>Latent heat of fusion:278 J/g Supercooling degree: 7.7°C</td>
<td>[24]</td>
</tr>
<tr>
<td>Na₃HPO₄·12H₂O (DSP)</td>
<td>Sucrose</td>
<td>1.5wt% DSP</td>
<td>Latent heat of fusion:223.1 J/g Supercooling degree: 1.54°C</td>
<td>[20]</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>Cus</td>
<td>1wt% Na₂HPO₄</td>
<td>Latent heat of fusion:202.4 J/g Supercooling degree: 3.5°C</td>
<td>[21]</td>
</tr>
<tr>
<td>Na₃HPO₄·10H₂O (TSPP)</td>
<td>Formamide</td>
<td>3wt% TSP PP</td>
<td>Latent heat of fusion:148.3 J/g Supercooling degree: 2.5°C</td>
<td>[22]</td>
</tr>
<tr>
<td>Chitin nanowhiskers (CNW)</td>
<td>None</td>
<td>1wt% CNW</td>
<td>Latent heat of fusion:241 J/g Supercooling degree: 11.1°C</td>
<td>[23]</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>CMC</td>
<td>0.8wt% α-Fe₂O₃</td>
<td>Latent heat of fusion:249.2 J/g Supercooling degree: 4.1°C</td>
<td>[25]</td>
</tr>
</tbody>
</table>
enhance both thermal and photon capturing characteristics of the SAT.

In this work, we demonstrate a facile method to synthesize a novel SSPCM material with enhanced thermal properties by incorporating modified SAT into the GNPs having different specific surface area values (300, 500 and 750 m$^2$/g) as supporting materials. The Sodium phosphate monobasic monohydrate known as SPM (Na$_2$HPO$_4$·H$_2$O) was used for the first time as nucleating agent and employed to promote crystallization of SAT. The effect of the nucleating agent on crystallization, melting temperature and enthalpy of fusion was investigated carefully by means of X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The hydrophilic GNPs were prepared by noncovalent functionalization of GNPs with 1-pyrene carboxylic acid to form hydrogen bonds with water molecules of SAT-SPM and greatly restrict the water molecular movement by providing a barrier against phase separation and fluidity of melted SAT-SPM. The SAT-SPM/GNPs form-stable composite PCMs were prepared via a physical blending and impregnation method, in order to simultaneously prevent leakage, suppress supercooling, maximize the light absorption, and enhance the heat transfer rate of SAT. The microstructure, chemical compatibility, supercooling suppression, thermal conductivity enhancement, heat storage behavior and thermal stability of the SSPCMs were analyzed in detail. The thermal cycling performance up to 500 cycles and photo capturing capability of the SSPCMS were also investigated. This work may provide a facile low-cost method for designing and synthesizing SSPCMs with great thermal reliability for potential applications in the field of solar thermal energy storage and conversion.

2. Material synthesis and experimental methods

2.1. Materials

Sodium acetate trihydrate; 99% (SAT, C$_2$H$_9$NaO$_5$) was purchased from WVR Chemicals, Germany. Sodium dihydrogen phosphate monohydrate (SPM, Na$_2$HPO$_4$·H$_2$O) served as nucleating agent was provided by Sigma Aldrich, Germany. Graphene nanoplatelets (GNPs, GRADE C) with different specific surface areas (300, 500 and 750 m$^2$/g) were obtained commercially from XG science, USA. For the fabrication of the GNPs, 1-pyrene carboxylic; 98% (C$_{17}$H$_{10}$O$_2$) was purchased from Sigma Aldrich, Germany.

2.2. Functionalization of the GNPs

Prior to experiments, GNPs with different specific surface areas were dried in an oven at 80°C for 24 h to remove free water on the surface. Noncovalent functionalized GNPs were obtained by sonicating GNPs (10 g) and 1-pyrene carboxylic acid (1 g) in ethanolic solution for 2 h, followed by overnight stirring at room temperature and washing process. The dried Hp-GNPs were collected after overnight drying in vacuum.

2.3. Preparation of the SAT-SPM-GNPs (SSG) composite PCMs

In the current study, the SSG form stable composite PCMs were prepared by a physical blending method using SAT-SPM eutectic mixture as PCM and Hp-GNPs with various specific surface areas as matrix material, solar absorber and thermal conductivity enhancer. At first, SAT-SPM mixtures with varying mass ratio of SPM were obtained by adding corresponding amounts of nucleating agent (0.5, 1, 2 and 3 wt %) into the pure salt hydrate. They were mixed in a sealed glass flask and heated to 75°C until complete melting and stirred for 1 h to obtain the clear SAT-SPM mixture. The mixture was cooled down and then mortar and pestle were used to grind samples by hand to provide SAT-SPM fine powder. The SSG composite PCMs were prepared via a solution impregnation method for Hp-GNPs with different specific surface areas (300, 500, 750 m$^2$/g) as shown in Fig. 1. Subsequently, the SAT-SPM powder with proper composition was added into a certain amount of Hp-GNPs (5 wt%). Then the resulting mixture was manually mixed and grinded following stirring for 1 h at 75°C. Finally, the resulting mixtures were cooled down and solidified at room temperature to obtain SSG composite PCMs. The optimal mass fraction of GNPs to achieve form stable PCMs were determined by preparing the SSG pellets and letting the excess SAT to be absorbed by filter paper at 75°C in closed glass jar.

2.4. Characterization

The JEOL (JSM-6010LA) scanning electron microscope was used for SEM imaging. The transmittance, absorption and reflectance spectra of the SSPCMs were measured using a UV–vis-NIR (PerkinElmer, Lambda950) spectrophotometer with wavelength accuracy of ± 0.1 nm. The crystallography analysis was investigated using the Bruker D2 Phaser desktop X-ray diffractometer with a Cu source for 2θ = 5 to 40°. The crystal morphology of the pure SAT and obtained SSPCMs were observed using a polarized optical microscope (POM, Axioskop 40POL, Germany) equipped with a high-resolution CCD camera. The phase change temperatures and enthalpy of fusion during the charging and discharging process for composite PCMs were obtained by differential scanning calorimeter (NETZSCH DSC 214 Polyma-Error ± 0.05% to ± 0.2%) at a heating rate of 2 °C/min. The weight loss and thermal stability of PCMs are examined by thermogravimetric analysis (TGA instruments TGA 550-Error 0.01%) for a temperature range of 50 to 400 °C and heating rate of 10 °C/min in purified nitrogen atmosphere. The Fourier-transform infrared spectroscopy was used to analyze the chemical composition of the samples in the wavenumber range of 4000–400 cm$^{-1}$ on a PerkinElmer ATR (Spectrum 100). Thermal conductivity of samples was measured by transient hot wire method using KD2 Pro thermal properties analyzer (Decagon Devices,USA) with a SH-1 probe. Prior to the measurement, the samples were compressed into cylindrical block with size of 25.4 mm x 30 mm using a made-home mold. Then, the blocks were located in 3D printed sample holder and temperature was controlled during the experiment using programmable thermal bath (Julabo-DYNEO 900F). The accuracy and the reproducibility for the measurement were within ± 5% and ± 2%, respectively. The accelerated thermal cycling test was performed to evaluate the thermal reliability of the prepared SSPCMs after 500 cycles. Thermal cycling test was performed for the temperature range of 30–75 °C and DSC analysis provided the enthalpy changes as well as heating and cooling curves after experiencing 100 and 500 cycles.

The light-to-thermal conversion performance was evaluated using a Sol3A Class AAA Solar Simulator(94023A, Newport,USA) with a 450 Watt Xenon lamp source and high flux beam concentrator that illuminated the (15 mm) diameter spot. The samples were placed in a thermal insulation sample holder where a quartz window covered the top of the cylinder and they were directly illuminated by a simulated sunlight source (~700 mW/cm$^2$). The temperature variations were also recorded using the a data logging unit (Omega-TC08).

3. Results and discussion

3.1. Effect of SPM mass fraction on nucleation of SAT

To investigate the effect of sodium dihydrogen phosphate monohydrate and (SPM) on the nucleation behavior and thermal characteristics of the sodium acetate trihydrate (SAT) composite, salt system, in detail. The thermal cycling performance up to 500 cycles. The accelerated thermal cycling test was performed to evaluate the thermal reliability of the prepared SSPCMs after 500 cycles. Thermal cycling test was performed for the temperature range of 30–75 °C and DSC analysis provided the enthalpy changes as well as heating and cooling curves after experiencing 100 and 500 cycles.

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solubility in molten SAT and its mass fraction play key roles in the acceleration of the crystallization rate within SAT-SPM salt mixtures. The low solubility of the SPM in molten SAT while having a hydrated structure provides a huge advantage over other nucleating agents such as disodium hydrogen phosphate (DSP), tetrasodium pyrophosphate decahydrate (TPD), anhydrous sodium acetate (SAA), sodium tetraborate decahydrate (STD) and sodium metasilicate nonahydrate (SMN) [39].

3.1.1. Phase change and supercooling behaviors of SAT-SPM

A daring goal is to provide low supercooling degree without extensive effects on the melting point and latent heat of SAT. The DSC curves of SAT-SPM with different SPM mass fractions are illustrated in Fig. 2 and in detail results were tabulated in Table 2. The DSC curves for SAT-SPM mixtures reveal a single peak, indicating the eutectic mixture of SAT and SPM. The DSC measurements were performed with low heating and cooling rate of 2 °C/min to suppress the effect of phase separation. Fig. 2(b-e) shows the melting and solidification curves of SAT containing different mass ratios of SPM. As shown in Table 2, the onset temperatures of melting ($T_m$) for SAT-SPM eutectic mixtures were decreased with the mass fraction increment of SPM. The phenomenon can be explained considering the interaction force debilitation of sodium acetate with H$_2$O molecules caused by Na$^+$ ions in SPM. When the mass fraction of SPM was higher than 1 wt%, the melting temperatures of the eutectic salt mixtures approached 54 °C and remained comparatively constant with a further SPM mass fraction increment. DSC measurements of two full cycles of melting and solidification were performed for better understanding of the phase change process in SAT and SAT-SPM mixtures. A significant enthalpy change was observed between the first and second melting cycles that can be attributed to the quality of thermal contact between the samples and aluminum pans or, to phase separation effects. The second cycle melting enthalpy value is in good agreement with reported values for pure SAT ($\approx$270 J/g)[40]. Building on these results, the supercooling degree of SAT-SPM mixtures with different SPM contents (0.5, 1, 2, 3 wt%) were 2.3, 0.2, 0.3, 0.7 °C, respectively (see Fig. 2f for details). From these results, it is evident that addition of SPM almost demolished the supercooling effect in SAT and reduced it by up to 0.2 °C. By taking into account phase change temperatures and supercooling degrees, the optimum concentration of SAT-SPM was estimated to be about 1wt% in SAT-SPM eutectic salt system. More importantly, the SAT-SPM-1wt% mixture represented a high latent heat of fusion (267.2 J/g) which was about 99 wt% of that of pure SAT (269.3 J/g).

3.1.2. Crystallinity and chemical compatibility of SAT-SPM salt system

The crystalline structures of SAT powder, supercooled SAT, SPM powder and SAT-SPM mixtures were analyzed by XRD and the resulting diffraction patterns are illustrated in Fig. 3a. The XRD pattern for SAT powder shows a sharp diffraction peak at 11.7° assigned to the feature peak (110) of SAT. The strong peaks at 16.9°, 22.5° and 29.7° attributed to the feature peaks (020), (221) and (402) of SAT, respectively. All diffraction peaks of the sample can be well indexed to the phase of SAT.
It confirms that SAT has mono-clinic crystal system in which the Na\(^+\) ion has distorted octahedral coordination with six oxygen atoms [41].

A new diffraction peak was observed for supercooled SAT at 8.8° due to the formation of sodium acetate (SA, CH\(_3\)COONa) molecules that is in good agreement with the orthorhombic crystal system of SA (JCPDS No. 29–1158). The presence or absence of hydrogen bonds within the SA and SAT crystals causes the largest crystal structure difference. Anhydrous sodium acetate has three crystal structures named as SA-I, SA-II, and SA-β which of the crystal structures are demonstrated in Fig. 3b [42]. The zoomed XRD patterns from 2\(θ\) = 8.2 to 9.4° in Fig. 3b represent the characteristic peak consistent with the (010) plane. Three asymmetric peak shapes are observed for SAT-powder, supercooled SAT and SAT-SPM-0.5% at 2\(θ\) = 8.78, 8.85, and 8.95°

advocating that all three crystal structures of SA crystallized concomitantly to form the CH\(_3\)COONa crystals within their solid structure. It can be seen that addition of SPM has an effect on crystallization products as only one diffraction peak for SA-II at 8.85° can be indicated for SAT-SPM-1% and SAT-SPM-2% while addition of more SPM changes products to SA-I and SA-II. The previous studies on crystal structure of SA suggested the stable form of the crystal for SA-II [43,44]. It is anticipated that formation of stable SA crystals leads to strong nucleation sites to achieve homogeneous nucleation. The initial liquid state such as temperature has shown considerable effect on kinetics of SAT crystallization. Moreover, a stronger SA diffraction peak at 8.85° compared with SAT peak at 11.7° is observed in the XRD pattern of the SAT-SPM-0.5% which can be evidence of the phase separation phenomenon. The SPM powder has very strong diffraction peak at 16.4° attributed to the

(JCPDS No. 29–1160). It confirms that SAT has mono-clinic crystal system in which the Na\(^+\) ion has distorted octahedral coordination with six oxygen atoms [41].

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_m) (°C)</th>
<th>(\Delta H_1) (J/g)</th>
<th>(T_m) (°C)</th>
<th>(\Delta H_1) (J/g)</th>
<th>(T_s) (°C)</th>
<th>(\Delta H_2) (J/g)</th>
<th>(T_s) (°C)</th>
<th>(\Delta H_2) (J/g)</th>
<th>Supercooling degree (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAT</td>
<td>58.1</td>
<td>298.6</td>
<td>58.2</td>
<td>269.3</td>
<td>-11.3</td>
<td>240.5</td>
<td>-5.3</td>
<td>230.2</td>
<td>63.5</td>
</tr>
<tr>
<td>SAT-SPM-0.5 wt%</td>
<td>56.9</td>
<td>297.1</td>
<td>56.5</td>
<td>256.1</td>
<td>54.7</td>
<td>251.7</td>
<td>54.2</td>
<td>249.6</td>
<td>2.3</td>
</tr>
<tr>
<td>SAT-SPM-1 wt%</td>
<td>55.8</td>
<td>292.3</td>
<td>55.1</td>
<td>267.2</td>
<td>54.9</td>
<td>261.3</td>
<td>54.9</td>
<td>260.6</td>
<td>0.2</td>
</tr>
<tr>
<td>SAT-SPM-2 wt%</td>
<td>55.7</td>
<td>290.3</td>
<td>54.1</td>
<td>261.8</td>
<td>53.9</td>
<td>261.2</td>
<td>53.8</td>
<td>260.6</td>
<td>0.3</td>
</tr>
<tr>
<td>SAT-SPM-3 wt%</td>
<td>55.6</td>
<td>288.4</td>
<td>54.5</td>
<td>261.6</td>
<td>54.35</td>
<td>262.1</td>
<td>53.8</td>
<td>259.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

\(T_m\), and \(T_s\): Melting and solidification onset temperatures for the first and second cycles \(\Delta H\): Enthalpy on DSC curve Supercooling degree = \(T_m\) (melting) - \(T_s\) (Crystallization)

Fig. 3. (a) XRD patterns (b) Zoomed part of XRD pattern for crystallization products of SA and (c) FTIR spectra of SAT, SPM powders and SAT-SPM with different mass fraction of SPMs.
(011) peak and that can be well indexed to the Orthorhombic phase of SPM (JCPDS No. 11–0651). Due to the low mass fraction of SPM, the SPM diffraction peaks are not recognizable in XRD patterns of SAT-SPM salt mixtures. The results from DSC measurement likely corroborate the XRD data by showing lower supercooling degree for SAT-SPM-1%.

The ATR spectra of SAT, SPM and SAT-SPM eutectic mixtures at room temperature are shown in Fig. 3c. For SAT powder, major peaks at 1350 and 1559 cm$^{-1}$ are caused by the C-OH and -C=O stretching vibrations affected by vibration coupling. The peaks at 3480 and 3280 cm$^{-1}$ can be assigned to stretching vibration of O-H group [18]. The peak at 780 cm$^{-1}$ corresponds to the deformation vibration of O-Na and the -CH$_3$ stretching vibration can be detected at 2916 cm$^{-1}$. These characteristics were also observed for the SAT-SPM mixtures. Meanwhile, the SPM showed a major characteristic peak of PO$_4^{3-}$ at 1100 cm$^{-1}$ that can be detected only at higher concentration of SPM. FTIR analysis is also in good agreement with XRD results indicating the physically fabricated SAT-SPM salt system without any changes in their chemical properties.

3.2. Shape Stabilized PCMs (SSPCMs)

Real-world applications of salt hydrate based composite PCMs for solar energy capture and storage requires a low degree of supercooling, high thermal conductivity and energy density, absence of phase separation, great photo-thermal conversion capability that need to be taken into consideration. An elegant forerunner towards these characteristics is proposed in this study by utilizing modified GNPs as a host matrix. The interesting properties of GNPs such as high thermal conductivity and specific surface area make them good candidates as host matrices for SAT-SPM salt systems. In this study three types of GNPs with different specific surface areas of 300, 500 and 750 m$^2$/g were considered to prepare shape stabilized SAT-SPM/GNP (SSG) composites. Previous studies have shown that the hydrophilic nature and good wettability properties of the host material can provide a great platform for crystal formation and suppress the supercooling and phase separation effects[45]. The hydrophilic GNPs were prepared by noncovalent functionalization of GNPs with 1-pyrenecarboxylic acid based on a previously reported method[46]. The functionalization of carboxylic acid groups(-COOH) as hydrophilic functional groups on the surface of GNP nanosheets was achieved via a nondestructive - stacking mechanism (aromatic interaction) as shown in Fig. 1. These functional groups do not dimerise in SAT-SPM, but form hydrogen bonds with water molecules of SAT-SPM and greatly restrict the water molecular movement providing a barrier against phase separation and fluidity of melted SAT-SPM.

3.2.1. Phase change and supercooling behaviors of SSPCMs

The DSC curves of SAT-SPM-1% and SSG composite PCMs during three cycles of the melting and crystallization processes are separately shown in Fig. 4 (a-c) and in details phase change parameters are listed in Table 3. Notably, the distinct difference between $\Delta H_m$ and $\Delta H_s$ that was observed most likely caused by the partial dehydration of the salt during the heating process. The SSG composite PCMs showed similar single peak as the SAT-SPM salt mixture. However, the phase change peaks became broader by addition of GNP nanosheets without considerable changes of melting and solidification onset temperatures ($T_m$ & $T_s$) which can be explained by the size distribution of the crystallites. It is anticipated that the GNP nanosheets will disturb the hydrogen bonds within the salt structure building up needle-like crystals that spread radially within SSG composites during crystal growth. Intimately linked, the crystal size will effect the melting and solidification temperature ranges. Moreover, SSG composite PCMs containing hydrophilic GNPs provided almost similar supercooling degree values compared with SAT-SPM. The hydrophilic surface of Hp-GNPs including carboxyl(COOH) groups provided the immense compatibility and wettability with the SAT-SPM mixture that boosted the attachment and offered heterogeneous nucleation for crystal growth of salt mixture on its surface. Advantageously, the strong interaction of carboxyl group with Na$^+$-CH$_3$COO$^-$ and H$_2$O molecules offers an intensive adherence between the ions and the crystals repressing the phase separation.

Furthermore, high energy storage capability of 230.8, 238.2, and 248.3 J/g were exhibited by SSG300, SSG500 and SSG750, respectively. The energy capacity of SSPCMs can be designated by two major thermal properties: impregnation ratio ($R_{imp}$) and impregnation efficiency($\eta_{imp}$) that are defined as:

$$R_{imp} = \frac{\Delta H_m, \text{composite}}{\Delta H_m, \text{salt}} \times 100$$

and

$$\eta_{imp} = \frac{\Delta H_m, \text{composite} + \Delta H_s, \text{composite}}{\Delta H_m, \text{salt} + \Delta H_s, \text{salt}} \times 100$$

where $\Delta H_m, \text{composite}$ and $\Delta H_m, \text{salt}$ indicate the melting enthalpy of SSG composites and SAT-SPM salt mixture, respectively. $\Delta H_s, \text{composite}$ and $\Delta H_s, \text{salt}$ represent latent heat of solidification for SSG composites and SAT-SPM salt mixture, respectively. The impregnation ratio ($R_{imp}$) specifies the salt content within the structure of SSG composites, and $\eta_{imp}$ indicates the effectual performance of impregnated SAT-SPM for latent heat storage. The theoretical impregnation ratio was calculated to be 95% considering the mass percentage of SAT-SPM that was added to prepare SSG composites. Nevertheless, the $R_{imp}$ for SSG composites has revealed lower values of 86.4, 89.1 and 92.9% for SSG300, SSG500 and SSG750, respectively. To some extent, the salt absorption capability of the Hp-GNPs is limited considering the capillary forces and surface tension of GNP nanosheets that are associated with their specific surface area. Furthermore, some portion of the liquid SAT-SPM was absorbed by filter paper from SSG pellets in the last stage of material preparation. The results stipulated diminutive differences of less than 1% between $R_{imp}$ and $\eta_{imp}$ for SSG composites determining the formation of highly crystalline salt on the surface of modified GNPs. The influences of confinement effects on the phase change enthalpy that

![Fig. 4. DSC melting and solidification curves of (a) SSG300; (b) SSG500; (c) SSG750.](image-url)
was reported in many studies was eliminated by introducing hydrophilic groups on the surface of GNPs [47], thus avoiding the discontinuation of hydrogen bonds within SAT-SPM salt mixture [48]. As was expected, the SSG750 attained the highest values for both $R_{\text{imp}}$ and $\eta_{\text{imp}}$ of 92.9 and 93.6%, respectively. That defines nearly all the salt crystals efficaciously store and release heat during a phase change process while dominating the volume alterations.

3.2.2. Chemical adaptability of SSPCM composites

The FTIR and XRD analyses were performed to further evaluate the chemical compatibility of SSG composites and results are shown in Fig. 5. The FTIR spectra of SSG composites represent the main characteristic peaks of SAT-SPM mixture without any changes or shifts confirming the physical interaction between modified GNPs and salt crystals with the dominant role of PCM. Moreover, the unchanged and strong band 3480 and 3280 cm$^{-1}$ (O–H stretching vibrations) specifies the compatibility between modified GNPs and salt mixture to maintain the covalent and hydrogen bonds between the water molecules and positively charged sodium ions of the salt. The XRD patterns of Hp-GNPs, SAT-SPM and SSG composite PCMs were shown in Fig. 5b. A single sharp diffraction peak at $2\theta = 26.41^\circ$ was observed in the XRD pattern of Hp-GNPs corresponding to the (002) crystalline plane of GNPs. The main diffraction peaks for both GNPs and salt mixture are visible in the XRD patterns of the SSG composites. The intensities of the salt crystal peaks were enhanced using GNPs in certain diffraction peaks suggesting the formation of highly crystalline salt on the surface of GNPs nanosheets. This result ratifies the physical interpenetration between GNPs and salt mixture to form shape stabilized composite PCMs in which the phase separation was eliminated.

3.2.3. Morphology and crystal structure of SSPCM composites

Toward a better understanding of morphology changes within SSPCMs, the SEM images of pure SAT, supercooled SAT, SAT-SPM and SSG composites are shown in Fig. 6. The smooth surface and rounded edges of SAT crystals are observed in Fig. 6a and b for SAT powders and supercooled SAT. A reduction in size and edge sharpness is observed upon addition of SPM into the SAT crystallites that is substantiated by XRD data with intensifying SAT diffraction peaks. Instead, a continuous and flat surface was found in SSG composites affirming that the interlayer surface of GNPs were covered by SAT-SPM forming shape stabilized composite PCMs. The specific surface area increment of GNPs in SSG composite has led to an enhanced capillary force between the surface of GNPs and molecules of SAT-SPM reducing the crystallite size into micro/nano crystallites and alleviating the leakage of PCM during the melting process.

POM characterization was performed for SAT, SAT-SPM and SSG composites and high magnification results are shown in Fig. 7. A highly crystalline morphology was observed with different crystal sizes and shapes during the solidification. Moreover, the high magnification images indicate the distinct changes in crystal sizes and shapes for SSG composites. It is conspicuous from Fig. 7c-e) that ultrathin needle like crystallites were formed without any definite orientation in SSG composites suggesting innumerable three-dimensional (3D) nucleation due to the lower surface energy near the GNPs nanosheets. An immense number of aggregates was observed for GNPs (750m$^2$/g) within the salt structure, stipulating that smaller GNP nanosheets provide a larger number of nucleation sites leading to a more potent heterogeneous nucleating effect.

3.2.4. Thermal and shape stability of SSPCMs

Shape stability is crucial to maintain a high energy density by hindering the leakage of molten PCM during the phase change process. Advantageously, the form stable structure provides consistent heat transfer properties along with the decrement of volume thermal expansion. To further investigate the shape stability of SSG composites, a leakage test was carried out visually as exemplified in Fig. 8(a-c). The powder samples were poured into glass containers and re-melted at 75 °C. Then, the glass containers were placed upside down as shown in Fig. 8b and subjected to a temperature of 75 °C for one hour. The SAT-SPM sample completely melted and leaked out while the SSG composites showed small traces of black particles that were not attached properly during the melting process. It is evident that Hp-GNPs provides a proper surface functionality and physical interaction to maintain shape stability during the phase transition process. Thermal stability of SAT, SAT-SPM and SSG composites were evaluated by means of TGA analysis and the results are illustrated in Fig. 8d. SAT has three water molecules in its structure (≈40% of the SAT molecular weight) that have completely vanished to form Sodium acetate when the sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$\eta_{\text{imp}}$ (%)</th>
<th>$R_{\text{imp}}$ (%)</th>
<th>Supercooling degree (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAT-SPM-1%</td>
<td>55.1</td>
<td>267.2</td>
<td>54.9</td>
<td>260</td>
<td>100</td>
<td>100</td>
<td>0.2</td>
</tr>
<tr>
<td>SSG300</td>
<td>54.9</td>
<td>230.8</td>
<td>54.6</td>
<td>220.7</td>
<td>85.6</td>
<td>86.4</td>
<td>0.3</td>
</tr>
<tr>
<td>SSG500</td>
<td>55.2</td>
<td>238.2</td>
<td>55</td>
<td>230.1</td>
<td>88.8</td>
<td>89.1</td>
<td>0.2</td>
</tr>
<tr>
<td>SSG750</td>
<td>55.1</td>
<td>248.3</td>
<td>55</td>
<td>245.2</td>
<td>93.6</td>
<td>92.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 3: DSC results for SSG composite PCMs with different specific surface area of Hp-GNPs.

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Fig. 5. (a) FTIR spectra and (b) XRD patterns of shape stabilized SSG composites.
has been heated up to 155 °C. Sodium acetate was further degraded at 450 °C into Na2O. For SAT-SPM and SSG composites, the thermal degradations happened in comparable steps as SAT. Further attention on the first degradation indicates that addition of GNP nanosheets delayed the dehydration process but not to a significant degree. The weight loss percentage of SAT, SAT-SPM, SSG300, SSG500 and SSG750 for desired working temperatures of 30 to 100 °C were 16%, 13%, 12%, 11% and 9.5% while the maximum loss rate occurred in the range of 70–80 °C. The small thermal stability increment for SSG composite PCMs shows that Hp-GNPs can act as thermal barrier to slow down the evaporation speed and confine the water molecules within the SSG structure by forming hydrogen bonds.

3.2.5. Solar-thermal conversion and storage performance of SSPCMs

The prime solar energy capturing, storage and heat transfer are the key frameworks to develop highly efficient photo-thermal conversion system. The thermal diffusion mechanism for photo-thermal systems was reported in some studies[49–52]. In this approach, solar photons are captured by the SSPCM surface and converted directly to heat raising the temperature of PCM indirectly by heat conduction within the composite structure. The photo-thermal performance of the PCM materials is directly related to their radiation absorption capabilities. Consequently, UV–vis-NIR spectroscopy was executed for precise measurement of transmittance and reflectance spectra to attain the detailed absorbance spectra as shown in Fig. 9. The AM 1.5 global solar spectrum is illustrated in the background of the graphs indicating the solar energy intensity or flux distribution at all wavelengths. Sunlight power is composed (by total energy) of about 5% ultraviolet light (below 400 nm), 42% visible light (400 to 700 nm) and 53% infrared light (above 700 nm) so the visible and NIR radiation accounts for 95%
of solar energy that is of great importance for solar-thermal applications. The transmittance spectra in Fig. 9a represent zero transmittance for SSG composites at all wavelengths while SAT and SAT-SPM samples transmitted some portion of the light. Interestingly, the reflectance spectra in Fig. 9b stipulates that SAT and SAT-SPM samples reflect some portion of NIR as well as 88 and 73% of the visible light, respectively. However, the SSG composites exhibited almost linear reflectance spectra data with low reflectance between 8 to 13%. The absorbance spectra confirm the low absorption of SAT and SAT-SPM in the UV and visible range plus some part of NIR region. The absorbance spectra of SSG300, SSG500 and SSG750 revealed the high solar absorbance of 86, 89 and 93% due to the excellent absorptivity of GNPs nanosheets. Among them, the SSG750 with higher specific surface area of GNPs provided better light absorption capacity that understood by the higher number of graphene nanosheets on the absorbing surface.

The photo-thermal energy conversion and storage performance of SAT, SAT-SPM and SSG composite PCMs was examined by locating the samples with the same weight and thickness inside the insulated holder with quartz window on top and exposing them to simulated solar illumination (AM 1.5) with a constant intensity of 700 mW/cm$^{-2}$ as shown in Fig. 10a. The temperature was recorded at the bottom of the sample by locating the thermocouple in the center for charging and discharging steps. Fig. 10(a) shows the graph for SAT indicating the slow temperature rise and gradually reaching the solid–liquid phase change then rising rapidly to the steady-state temperature of about 80 °C which takes about 1620s. Subsequently, by turning off the incident light, the temperature of the SAT decreases rapidly while the energy is discharged by triggering nucleation confirming the supercooling phenomenon. In contrast, the releasing stage of the stored heat for SAT-SPM and SSG composites can be detected without supercooling effects in Fig. 10(c-f). Two charging and discharging cycles with dissimilar final temperature of 80 and 75 °C were performed for SAT-SPM and SSG composites to evaluate the effect of working temperature on their photo-thermal performance and efficiency. Furthermore, as can be
seen clearly from the graphs, the SSPCMs showed significant improvement in photo-thermal performance of SAT-SPM salt mixture by reducing the charging time to almost one-third, from 1176s (SAT-SPM) to 424s (SSG300). The photo-thermal performance of SSPCMs was further evaluated by calculating the photo-thermal efficiency based on the temperature graphs and DSC results for the PCMs[52]:

\[
\eta = \frac{Q_T}{G_s A t}
\]

where \(G_s (W/m^2)\) is the solar flux, \(A (m^2)\) is the irradiation surface, \(t (s)\) is
the irradiation time and $Q_T(J)$ is the heat storage capacity of PCMs calculated by:

$$Q_T = m \int_{T_{25}}^{T_f} (C_p + \beta \Delta H) \, dT$$

(4)

where $m(kg)$ is the mass, $C_p(kJ/kg.°C)$ is the specific heat capacity, $\beta$ is the melting fraction, $H$ is the latent heat, $T(°C)$ is the temperature, $T_{m(onset)}$ and $T_{m(endset)}$ are the melting on and endset temperature of PCMs. The specific heat capacity was considered to be constant at 2.7(kJ/kg.°C)[15]. The photo-thermal efficiencies at 40, 60 and 70 °C are demonstrated in Fig. 11a for different PCMs. It can be realized that the maximum efficiency was achieved at 60 °C where the phase transition completed due to the rapid increase in heat storage capacity. Consequently, SSG composites have shown considerable high solar-to-thermal energy storage efficiencies of 87.2–92.6% at 60 °C that were decreased to 70.2–73.1% at 70 °C owing to higher thermal losses to their surroundings at higher temperatures. The efficiency calculations from two heating cycles with different final temperatures showed a small variance of less than 5% suggesting the good photo-thermal reliability for prepared SSPCMs. Indisputably, the prepared salt hydrate based SSPCMs simultaneously possess high energy density with an excellent solar thermal efficiency nominating them as very promising materials for solar energy applications.

### 3.2.6. Thermal conductivity and reliability of SSPCMs

Precise information of a material’s thermal conductivity is crucial in heat transfer applications as well as composite PCMs. Importantly, thermal conductivity directly reflects charging and discharging rates of SSPCMs by altering the heat transfer from the heat source to the SSPCM and from the SSPCM to its nearby surroundings. Fig. 11b presents the thermal conductivity values for SAT, SAT-SPM and SSG composite PCMs at 30 °C. The pure SAT and SAT-SPM exhibit low thermal conductivity values of 0.65 and 0.71 W/m.K, respectively. The addition of Hp-GNPs had a significant effect on the thermal conductivity of SSPCMs by enhancing the conductivity up to 2.71, 2.38 and 2.14 times higher than that of the SAT-SPM for SSG300, SSG500 and SSG750, respectively. Undeniably, the high intrinsic thermal conductivity of GNPs can significantly enhance the thermal conductivity of SSPCMs by offering an interconnected graphene nanosheets heat transfer network within the salt structure. The SSG300 composite PCM offered the highest thermal conductivity which can be attributed to higher GNPs loadings or having a larger lateral size and thickness that reduces the phonon scattering at the matrix-bounded interface and results in an effective improvement in the thermal conductivity and heat dissipation ability of the composite[53].

The assessment of physical and chemical stability is very important when considering the prepared SSPCMs for practical applications. Consequently, the thermal reliability of SSPCMs was appraised by utilizing the accelerated thermal cycling test[54]. A DSC measurement was performed to evaluate the variation of supercooling degree, latent heats of melting and crystallization after 100 and 500 cycles as tabulated in Table 4.

The supercooling degree values of SSG composites after 100 and 500 cycles are almost equivalent to the initial values for uncycled samples. The TR numbers indicate the high thermal reliability of the SSPCMs in terms of energy density after a large number of thermal cycles. The results indicate slight fluctuation of 3.2, 0.3 and 0.7% for SSG300, SSG500 and SSG750 samples, respectively. The crystal order may not be restored to form the initial crystal configuration during the cycling test which can explain the slight change in thermal storage performance of composite PCMs. However, substantial changes were observed for the SAT-SPM salt mixture which were evidently caused by incongruous melting and phase separation upon cycling. Minor variations in the supercooling degree, phase change temperature, and latent heat values urge the utilization of the prepared SSPCMs for low-temperature latent heat storage applications, such as solar thermal energy storage and waste heat utilization.

#### 3.2.7. Potential application of SSG composites

The SSPCMs with high latent heat of fusion and phase transition temperature of about 60 °C are well qualified for low-temperature thermal energy storage systems. The intermittency nature of solar radiation for solar driven applications including solar-thermal heaters and solar cookers provides vast opportunities for SSPCMs to reduce the gap between supply and demand of energy. The SSPCMs are able to store the suppress solar energy and provide the thermal energy for off-sunshine hours. In a similar fashion, they can be utilized for waste heat recovery systems to store extensive amounts of waste heat to be used in later time periods for indoor or space heating. In addition, the SSG composites prepared in this study have shown superior thermal properties compared with other reported salt hydrate based SSPCMs as shown in Table 5. The SSG composites offer much higher latent heat and impregnation ratio while the thermal conductivity is comparable or even superior to those previously reported in literature. Meanwhile, the improved thermal stability and persistent fire resistance make them more competitive compared to other organic PCMs. Building on these results, the SSG composites are recommendable SSPCMs for future thermal energy storage applications such as solar-thermal collectors, thermal management and waste heat utilization. However, further work is still needed to put SSPCMs into practice and to take full benefit of their superior properties.

### 4. Conclusion

Cheap and scalable photo-driven SSPCMs were fabricated based on modified hydrated salt PCM grafted hydrophilic GNPs. The SPM was used to suppress the supercooling degree and maintain a high energy storage capacity for SAT-SPM salt mixtures. The hydrophilic GNPs were prepared by noncovalent functionalization of GNPs with 1-pyr-encarboxylic acid to form hydrogen bonds with water molecules of SAT-SPM that largely restricted molecular movement of water, thus...
providing a barrier against phase separation and fluidity of melted SAT-SPM. This augments the deficiencies of SAT including phase separation, leakage in molten state, low thermal conductivity and shortage of solar energy capturing and storage. The SPPCMs offered a superb thermal energy storage capacity (230.8–248.3 J/g) and enhanced thermal conductivity from 0.65 (W/m.K) for pure SAT up to 1.93 (W/m.K) which is attributed to the high thermal conductivity of graphene nanosheets. Advantageously, the shape stabilized SSG composites showed great thermal reliability and shape stability together with excellent photo thermal efficiency of 92.6%. Given that, we study a novel SPPCM composite PCMs with enhanced thermal performance for solar energy utilization and thermal management.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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