



Light Energy Conversion and Storage by Phase Change Materials



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Abstract

There are constant efforts to minimize the energy load by using phase change materials (PCM). The development of PCM has reached a stage where the applications can be planned with desirable properties. Together with development of PCM strategies one parallel area is slowly growing, which is the use of PCM and its nanocomposites for tapping solar energy in addition to the existing photovoltaic solar cells. There are some efforts to commercialize the technologies. More and more efforts are being done to store the thermal energy by using molecular strategies. The present paper discusses some of the developments in the area of tapping light energy for generation of heat and its storage.

Introduction

The foot prints of carbon and greenhouse gases by the use of the conventional resources leads to create health, environmental and other socio- economic problems throughout the world [1]. The waste heat is available everywhere, from industrial processes, to solar heat, and even the heat coming out of vehicles. The heat just wasted can be recycled by using phase change materials. Thermal energy storage offers enormous potential for a wide range of energy technologies. Solar energy with abundant nature is the only renewable energy source that can replace fossil fuels to maximum possible extent [2-5].

As a result, the research and the development of sustainable solar energy conversion and storage technologies has attracted constantly growing interest. Among other factors, the efficiency of energy conversion and storage depends on the structure and property of the materials used [6,7]. Various prospective nanomaterials have been studied for their energy conversion efficiency and storage of solar irradiation [8,9] Photoinduced nanocarbons, driven by sunlight, are one of the most attractive materials in modern chemistry [10-12].

There are efforts to utilize the PCM as an energy storage system and the energy is harvested from sunlight. Excess heat from sunlight is already being utilized. The use of PCM will make the system store the abundant energy more efficiently.

Photo-Thermal Energy Conversion

The conversion of abundant solar energy in to usable form of energy motivated many research activities including utilization

phase change materials, which can store energy during exposure to sunlight and utilize at night. Many researchers have attempted to establish the conversion of light energy to heat and its storage.

PCM Performance Under Sunlight Irradiation

Single walled carbon nano tube (SWNT) based systems

The SWNTs are used as a nanoscale photon antenna, which acts as an effective photon capturer and molecular heater of the light-to-heat conversion process. The optical absorptions of SWNTs are due to resonant band-to-band transitions [13] and π -plasmon excitation [14-16] PEG also absorbs the near-infrared light of the solar irradiation [17]. Also, the SWNTs form SWNT/PCM composites having high thermal conductivity that shorten the heat storage and release time [18,19]. Obviously, this composite is able to harvest visible light and convert it to thermal energy much more efficiently as compared to the traditional organic PCM for latent heat thermal energy storage [20,21]

During solar irradiation, the SWNTs of the SWNT/PCM composites do rapid UV-vis sunlight-harvesting and light-thermal conversion, while the generated thermal energy is stored in the PCMs by a form-stable phase transition with a high energy storage density [22]. These sunlight-driven SWNT/PCM composites are qualified for important potential application as renewable and clean energy sources.

Single walled nanotube (SWNT) is blended with polyethylene glycol 10000 (PEG 10000)-co-N, N'-dihydroxy ethyl aniline to be used as a form-stable polymer PCM (SWNT/PCM) composite [23].

The SWNT/PCM composites exhibit several smart features, such as latent heat storage with high energy storage density, excellent flexibility, high light-to-heat and energy storage efficiency ($\eta > 0.84$). Above features advocate the use of SWNT/PCM composites for smart clothing or leather through fabric blending or wire drawing. Also, the composites, having strong near-infrared absorbance characteristics and high energy storage density, have a potential

application in military stealth. Carbon nanotube sponge (CNTS) can be used as a porous scaffold to encapsulate paraffin wax (PW), which makes an electrically conductive composite with enhanced phase change enthalpy and thermal conductivity (Figure 1) [24]. This composite has practical importance due to its ability for efficiently storing thermal energy from electro heat conversion or light absorption.

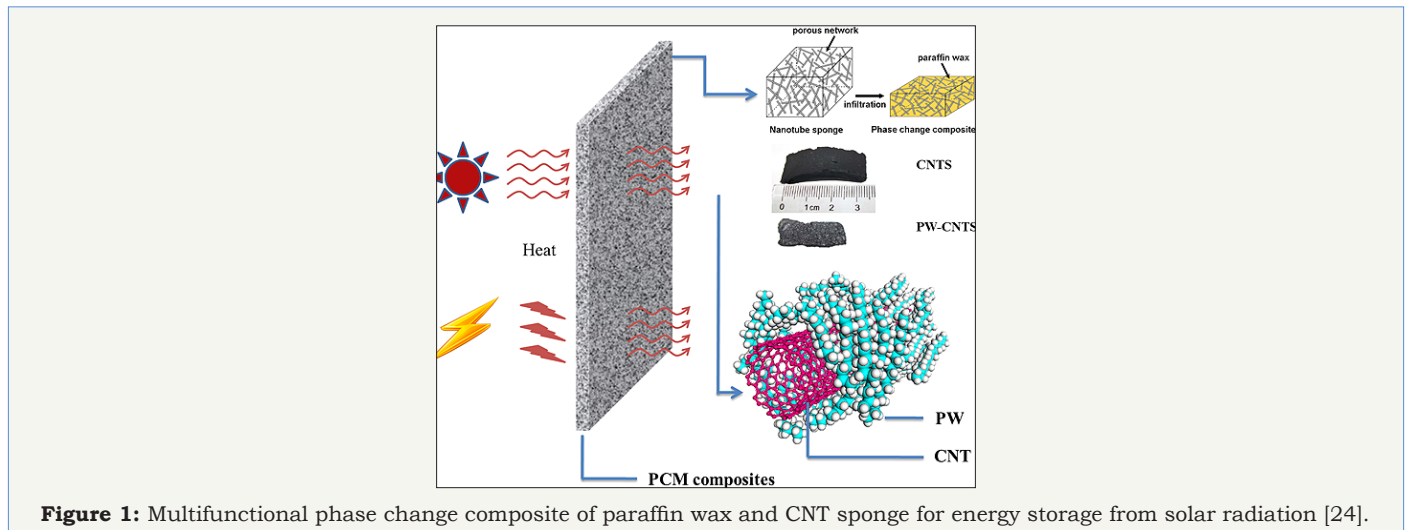


Figure 1: Multifunctional phase change composite of paraffin wax and CNT sponge for energy storage from solar radiation [24].

The presence of nanotubes enhances photon absorption, which heats the PW in the composite. Under simulated solar illumination at controlled intensities of 58, 70, and 90 mW/cm² the surface temperature of a blank CNTS increases abruptly from 15 °C to more than 30 °C that reaches equilibrium over a period of 400s. When a PW/CNTS composite (87wt.% loading) is exposed to light,

phase change occurs at temperatures close to 25 °C under all light intensities, which can be seen from the reduced slope and inflection point in each curve (Figure 2) [24]. The heat is released from the composite during the cooling of PW after turning off the light. Composites have energy storage efficiencies of 40% to 60% which increase with higher light intensity.

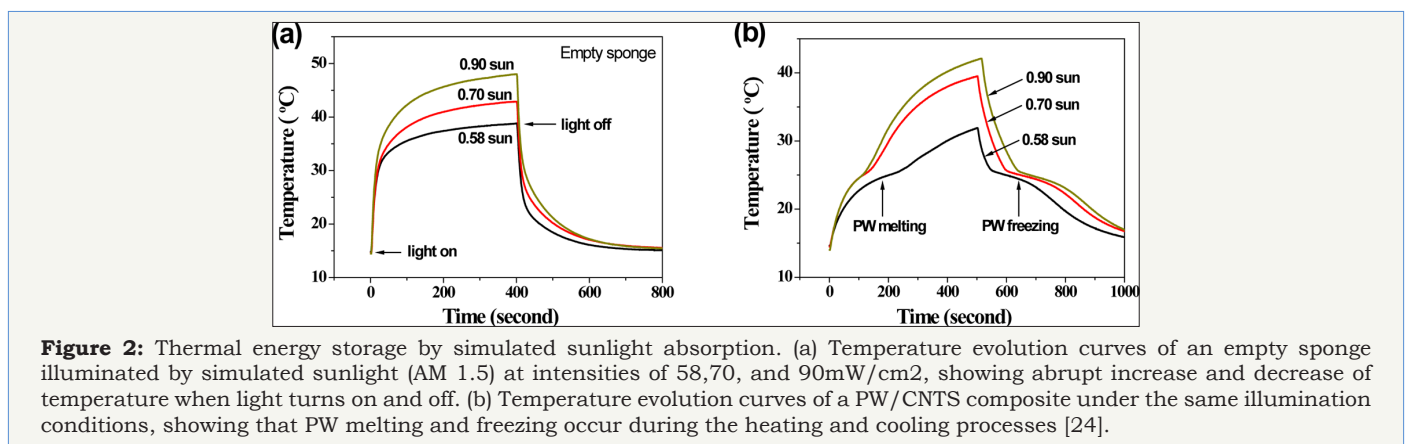


Figure 2: Thermal energy storage by simulated sunlight absorption. (a) Temperature evolution curves of an empty sponge illuminated by simulated sunlight (AM 1.5) at intensities of 58, 70, and 90 mW/cm², showing abrupt increase and decrease of temperature when light turns on and off. (b) Temperature evolution curves of a PW/CNTS composite under the same illumination conditions, showing that PW melting and freezing occur during the heating and cooling processes [24].

Graphene based systems

The GO sheets can easily be functionalized via covalent linkage to control its physical and chemical properties for different applications [25]. Thus, oleyl amine functionalized reduced graphene oxide (OA-rGO), used for shape stabilization, absorbs palmitic acid to make shape stabilized composite. The connected graphene network provides nuclei for the heterogeneous nucleation and crystallization of PA and also provides enhanced heat transfer while maintaining excellent shape stability. The black surface of

OA-rGO facilitates capturing the photon energy and heating the PA molecules, which store the thermal energy via phase transition. Similar to heating rate, the cooling rate for PG (PA+GO) composites is higher than for pure PA due to the enhanced thermal conductivity of the composites (Figure 3). Under microwave, the expansion of GO layers (4 wt%) in presence of PEG ensures superior blending leading to heat storage capacity of 174.5 J/g, almost equal to the phase change enthalpy of pure PEG. [26].

A typical nanocomposite shape stabilized PCM [Polyethylene glycol/graphene oxide, (PEG/GO)] absorb energy during the light radiation, which raises its temperature [28]. When the temperature reaches the melting point of PEG, an inflection point appears that indicates the onset of phase change. After removal of the lamp at the temperature of about 60 °C, it was allowed to cool and release heat. However, there is slight rise in temperature, which is accounted for the released energy and there is decrease of temperature after that. The curves can be divided into two parts which represent melting and crystallization progress respectively. Further insight

in to the process reveals that the pristine PEG melts much slowly and crystalize very fast. The introduction of GO into the composite enhances the absorption of the light, which ensures fast melting process. During the crystallization part, the released energy raises the sample's temperature due to re-absorption of energy by PCMs composites. Thus, the thermal absorptivity is enhanced to considerable extent due to small amount of GO and also, it provides a better performance in photo-energy absorption and form-stability. The overall effect is the better utilization of energy.

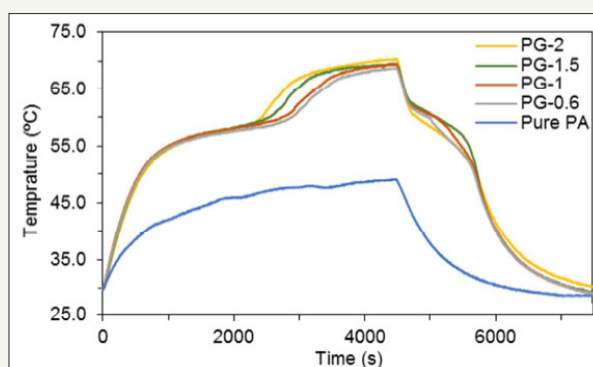


Figure 3: Obtained temperature of Pure PA and PG composites (light irradiation, ambient temperature 28 °C) [26].

Hybrid graphene aerogels (HGA) comprising GO and graphene nanoplatelets (GNP) were prepared and introduced into polyethylene glycol (PEG) via vacuum impregnation to obtain composite PCMs having superior properties along with the ability for light-to-heat energy storage [27]. In order to optimize its solar energy storage and release, the light-to-heat energy conversion experiments were carried out on the composite PCM using solar irradiation. The general characteristics remain similar to that observed by Xiong et al. [26]. As compared to PEG/HGA composite PCMs, the pure PEG has a white surface that would reflect the irradiating light, which meant that the PEG could not reach its melting point and realize the solar energy storage. Thus, the composite PCMs based on HGA had better performance in light-to-heat energy conversion. The light-to-heat and energy storage efficiency of the composite PCMs can be calculated by using photothermal calculation [36]. The energy conversion efficiency of the composite PCMs varies in the range of 80-90%.

Graphitic foam (GF) fabricated by CVD is a monolith of a graphene 3D network, which paves the way for phonon transport with small resistance through the high-quality and continuous CVD-grown graphene building blocks [28]. This continuous GF monolith with a high basal-plane solid thermal conductivity of graphene is blended with a PCM to act as a thermal conductive filler with ability for phonon transport [29].

However, the pore size of GF being hundreds of micrometers with low density the thermal resistance of the heat transfer from the PCM inside the large pore to the GF strut walls is obviously large. Therefore, the improvement of the thermal conductivity of the composite PCM is done by growing a network of CNTs inside the pores [30]. In another approach the conductive path

of GF is increased by filling the large pores of GF with a denser interconnected hollow graphene network (HGN). The obtained GF filled with the HGN [hierarchical GF (HGF)] is integrated with paraffin wax (PW) via vacuum impregnation to obtain a PW/HGF composite PCM. The HGF functions as a photon antenna that realizes photon capture and light-to-thermal energy conversion. Therefore, with solar irradiation the PW/HGF composite PCM can harvest solar energy and convert it to thermal energy, which is then stored in the composite PCM with high energy storage density. The PW/GF and PW/HGF composite PCMs absorb over the whole UV-vis-NIR range, while the pure PW shows no absorption peak in the visible-light range. The black color of the HGF allows it ideal light absorbance, which enhanced the photo-absorption of the composite PCMs [31]. The thermal energy storage efficiencies of PW/GF and PW/HGF composite PCMs are high at around 88-89%.

Phase Change Material Based Domestic Solar Cooking System

Solar thermal energy can be stored during sunshine hours by using various techniques which can be used during off sunshine hours effectively for useful purposes. Kenisarin & Mahkamov [32] conducted various studies using different phase change materials which are useful for active and passive solar space heating and cooling and solar cooking applications [35]. The PCM developed for solar application was based on tube, filled with PCM, which was exposed to sunlight and the molten PCM is used for cooking by designing hot plate [33]. The heat transfer enhancement in latent heat thermal energy storage was attempted by Merlin by using conductive structures like finned exchangers, graphite powder and expanded natural graphite (ENG) [34]. Practically, heat exchanger tube and the outer annular of the heat exchanger, filled with PCM,

make the system. The PCM incorporated in ENG matrix is the best storage configuration for industrial purposes with the overall heat transfer coefficient around $3000\text{Wm}^{-2}\text{K}^{-1}$ and the thermal conductivity 100 times more than that of PCM alone. The solar cooking system comprising a solar concentrator in the form of parabolic dish and a receiver or cooking pot, which is placed at the focal point of the parabolic dish, performs well with high absorption of solar radiation [35].

PCMS Used in Photovoltaic Modules Thermal Management

It is known that part of the solar energy absorbed by a photovoltaic cell is converted into electrical energy while the rest is wasted as heat that increases in the temperature of the solar cell [36]. In fact, the operating temperature of a photovoltaic device could reach as high as $80\text{ }^\circ\text{C}$ at high solar radiation intensity [37]. The open-circuit current increases at elevated temperature but is associated with a decrease in open circuit voltage. The overall effect of changes in current and voltage causes a reduction in the output power of PV cells. Jiang et al. [38] observed that the maximum output power of PV modules under 1000Wm^{-2} could decrease from 240W to 196W as the temperature is raised from $0\text{ }^\circ\text{C}$ to $75\text{ }^\circ\text{C}$ [39]. The PCM-based thermal management systems are considered to be effective in controlling the temperature of photovoltaic modules and reducing the loss of photoelectric conversion efficiency. According

to the prediction from simulation, using realistic one-day weather conditions, the maximum temperature of the front surface of the system with PCMs remains below $34\text{ }^\circ\text{C}$, which helped in achieving high electrical conversion efficiency.

Storage of Energy by PCM Having Molecular Interaction with Photoactive Molecule

The sensitivity of phase-transition to the temperature of the surrounding prevents the long-term storage of latent heat without loss to the environment remains a challenge [40]. The preventive action against spontaneous heat loss can be the installation of an energy barrier for the reverse-phase change from a high-energy phase to a low-energy phase. However, the installation of common energy barrier by using mechanical triggering is limited by the high cost for large-scale applications. Phase changes are influenced by intermolecular interactions, such as van der Waals, dipolar, and hydrogen bonding, which indicate that the phase-transition temperatures and thermal energy densities can be controlled by regulating these key interactions between constituents. Organic photo switches that undergoes reversible isomerization under irradiation of light can be integrated with various materials for smart applications. It is expected that this property can be utilized to alter the physical properties of surrounding molecules through the change in intermolecular interactions.

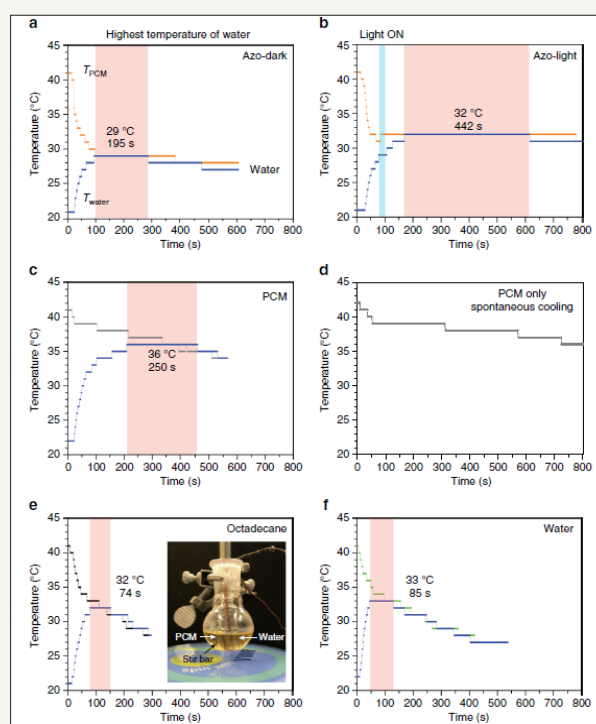


Figure 4: Water-heating experiments. Showing the temperature changes of 1g of water (blue curve) in contact with 3g of (a), ultraviolet-charged phase-change materials (PCM) composite (35mol% of cis azobenzene dopant (compound 1)) in the dark. (b) Optically triggered composite by the exposure to a blue light emitting diode lamp at $31\text{ }^\circ\text{C}$ for 500s to maximize the discharging of cis azobenzene, (c) pristine PCM (i.e., tridecanoic acid), (e) octadecane, and (f) water bath. The inset of (e) shows the setup where each thermocouple is submerged in a heating medium and in a vial containing water. The temperature of water in the vial is at $21\text{--}22\text{ }^\circ\text{C}$ under ambient condition and quickly increases as the vial is immersed in the heating medium at $40\text{ }^\circ\text{C}$. The temperatures of the heating medium (T_{PCM}) and water (T_{water}) are recorded simultaneously after T_{PCM} reaches $41\text{--}42\text{ }^\circ\text{C}$ while the heating fluid is stirred. (d) Temperature change of pristine PCM under ambient condition without the process of dipping a water container into the PCM heating bath.

Thus, the doping of azobenzene into conventional organic PCMs can be considered as an approach to change the intermolecular dynamics. These dopants have activation energy barriers for switching between the photo isomers, which provide stability to the phase storing thermal energy and ability for energy release. Thus, high-density energy storage is controllable and scalable in organic composites. Specifically, the azobenzene dopants that change conformation upon illumination can be locked in the liquid phase of PCMs by lowering their crystallization temperature (T_c), retaining the thermal energy storage at cooler temperatures [41]. The heat released by optically triggered UV-charged PCM composite is transferred to water, whose temperature can be seen in Figure 4.

For example, with n-fatty acids having -COOH groups, the polar interaction and H-bonding between the acid groups can impact the lamellar formation. The azobenzene dopants possess strong π - π interactions among adjacent aromatic cores and van der Waals interactions between alkyl chains. Ester linkers are also expected to contribute to intermolecular interactions.

In the first stage of the thermal storage cycle, the external thermal energy is absorbed by the solid composite in crystalline state. Above the melting point (T_m) of the PCM (42 °C), the composite becomes a mixture of molten PCM and crystalline aggregates of the azobenzene dopant, which has a higher melting point of 73 °C. Then during UV illumination of the slurry, the trans azobenzene dopants isomerizes to cis, which having bent conformation remains well dispersed in the liquid PCM. To keep the temperature of the composite above 42 °C during the UV-charging process, simultaneous heating and UV absorption processes are adopted [42]. The total heat stored by liquid composite comprises the fractional latent heat of the PCM (177Jg⁻¹), that of trans azobenzene dopants (118Jg⁻¹), as well as the fractional isomerization energy of the metastable cis azobenzene (116Jg⁻¹). It is also observed that the liquid state of the composite is conserved through subsequent cooling to a temperature. Unusual heat storage ability of the composite is achieved by the metastable cis-dopants that does not allow the packing of PCM molecules through steric repulsion and dipolar interactions. Visible-light illumination rapidly isomerizes the dopants back to trans state and allows the PCM composite to crystallize and release the stored latent heat as required, recovering the original state of the composite.

Conclusion

Attempts are being made to utilize suitable PCM composite with carbon-based Nano materials to tap solar energy and store it to mitigate the over dependence on electricity. Carbon based Nano materials such as SWNT, GO, rGO etc. found to be ideal materials which make shape stabilization possible with very low dose incorporation in PCM. Nano carbons are responsible for absorption of photon from sunlight and PCM acts towards storage. Further, the physical blending allows minimum surrender of original enthalpy of PCM and the other important characteristics is the high thermal conductivity of nanocarbons, which makes the system to respond very fast. The search for most suitable material combinations has just started. This is expected to yield rich dividend in near

future as more efficient materials will be developed with umpteen combinations.

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