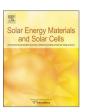
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Di-functional nanocomposite films for efficient conversion and storage of solar energy



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ABSTRACT

There is no doubt that renewable sources, such as solar energy, have played an important role in the future renewable energy system. And solar heat has great potential and a high contribution towards the future energy supply. How to directly collect, fast convert and efficiently store solar heat is still a problem to be solved in solar energy application. Herein, the di-functional nanocomposite film was designed and fabricated toward efficient conversion and storage of solar thermal energy. The di-functional nanocomposite film was feasibly prepared by uniformly imbedding phase change materials (PCMs) and Au nanoparticles into PVA matrix uniformly through the hydrogen-bonding interactions. The Au nanoparticles, as photothermal nanoabsorbers, with a low concentration (~0.23% m/m), can instantly and intensely realize solar-to-heat conversion by utilizing surface plasmon resonance. Subsequently, efficiently conversion heat could be stored into the PCMs through film-interior reversible phase transformation. Meanwhile, no leakage and evaporation of the PCMs is observed due to the strong hydrogen-bonding confinement at interface between PCMs and the film matrix. This kind of difunctional nanocomposite films is of great importance and wide usage in the fields of solar thermal energy conversion and storage, thermal interface materials, protective layers and sensing, etc.

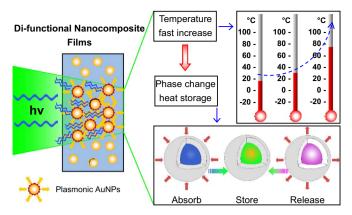
1. Introduction

Efficient conversion and storage of solar energy is particularly attractive since the solar power is the most plentiful, clean and lasting renewable energy source [1]. Utilization of solar energy is considered to be the most promising technology in the future energy system, in which solar heat has great potential in future solar energy usage [2]. The key is how to directly collect, fast convert and efficiently store the solar thermal energy for the further application. Plastic thin films, such as protective films, are excellent materials for solar thermal applications in agriculture due to their ability to regulate solar/heat transmission [3–5]. In recent years, to improve light absorption, some efforts have been made to improve light absorption by doping photo-selective additives in plastic materials during the process of conversion of solar energy. For example, organic dye molecules were integrated into poly (ethylene glycol) matrix to collect, absorb and convert visible light into heat [6-8]. Meanwhile, to improve the overall thermal conductivity of solar thermal thin films, high thermal conductivity fillers, including metal/metal oxide particles [9,10] and a variety of carbon materials [11–15], were used considering that these fillers can accelerate the thermal diffusion from light absorber [16-20]. The inherent defects of thermal thin films, such as low thermal conductivity and low thermal storage, may restrict its partial practical application. Therefore, a well-designed di-functional nanocomposite films toward fast solar-to-heat conversion and their efficient storage of solar energy is remained in urgent demands.

Herein, different from previous work, we designed and fabricated a di-functional nanocomposite film by combining rapid photo-thermal conversion and efficient thermal storage. The photothermal effect of Au nanoparticles (Au NPs) is attributed to the plasmon resonance, which speeded up the heating rate of organic plastic film matrix. Meanwhile, illuminating this kind of film by sunlight or a low-power pulsed laser, the generated heat could be charged into PCMs for storage. What's more, the PCMs exhibit a highly film-interior reversible phase change, in which neither leakage of PCMs nor change of film shape is observed due to the strong hydrogen-bonding confinement between PCMs and the matrix. Compared with ordinary films, the thermal storage efficiency of the di-functional nanocomposite film was enhanced by 201%, exhibiting an outstanding ability to store thermal energy. The current obtained di-functional nanocomposite films have great poten-

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Scheme 1. The design concept of the di-functional nanocomposite film combining rapid solar-to-heat conversion and thermal storage and release.

tial in wide application fields involving photo thermal energy conversion and storage.

Firstly, the design concept we proposed is illustrated in Scheme 1. The Au NPs were chosen as photothermal nanoabsorbers, in that the incident light excites Au NPs to transfer energy to lattice vibrations on a picosecond timescale. As a result, energy absorbed at or near the plasmon resonant frequency is rapidly converted to heat [21–23]. It is a prerequisite for fabricating a film with rapid photothermal conversion. The Au NPs of small size were confirmed to have the best performance of photothermal conversion efficiency and conversion stability compared with other materials at the same conditions, including PbS NPs, organic dyes and carbon black [24]. Secondly, PCMs can store and release more latent heat than other sensible heat materials. Therefore, the ability to absorb heat from environment offers a strong thermal energy function [25].

2. Results and discussion

2.1. Structure of the films

To achieve and obtain a homogeneous di-functional nanocomposite film, Fig. 1A describes the simple procedure for fabricating the difunctional films. Spherical Au NPs were synthesized by coating citrate ions as the stabilizing agent [26] and used as numerous photothermal nanoabsorbers to fast convert solar energy to thermal energy (Experimental Section S1.2, Supplementary materials). The obtained Au NPs can be easily dispersed into PVA solution (1) due to the

effective surface protection of citrate ions. The strong hydrogen-bond interactions between the carboxyl groups of citrate ions and the hydroxyl groups of PVA molecules, will thus drive the selective hostguest interaction at the surface of the Au NPs. As PEG molecules (2) were added into above suspended solution, PVA molecules also played the role to form hydrogen-bond with C-O groups (the ether bond) of the PEG molecules simultaneously. Herein, the hydrogen-bond from interaction of PEG and PVA molecules can tightly lock phase change PEG molecules and prevent leakage after phase transition. (The hydrogen-bond interactions were characterized using IR spectroscopy. as shown in Fig. S2, Supplementary materials). The TEM image of Fig. 1B shows that the synthesized Au NPs are near monodisperse and spherical with an average diameter of ~25 nm (particle size distribution histogram was shown in Fig. S3, Supplementary materials). The mixing solutions were highly stable and homogenous. As the concentration of Au NPs increased, the color of solutions changed from colorless to pink to dark red gradually (Fig. 1C). UV-Vis spectra (Fig. S4, Supplementary materials) show the same absorption peak centered at 532 nm and the peak intensity increased with the increasing concentration of Au NPs. Finally, the relevant di-functional nanocomposite films were made by facial drying under air/vacuum condition (Fig. 1D). The color of the obtained films was similar with the color of the mixing solutions and the di-functional nanocomposite films exhibit high optical transparency. Those results indicated that the Au NPs were equally distributed into PVA matrix. No aggregation of Au NPs is critical for both penetration of incident light source and the highefficiency excitation of plasmonic nanoparticles.

2.2. Laserlight-to-heat conversion

Before solar-to-heat conversion measurements, the photothermal properties of the obtained di-functional films were systemically studied to deeply understand the essence of utilizing surface plasmon resonance to quickly implement photo-to-heat conversion and efficiently charge thermal into PCMs. As is well known, when the Au NPs size matches the plasmon wavelength, a strong and resonant excitation of surface plasmon can be produced quickly to generate heat [22,23]. A green low-power pulsed laser (~532 nm of wavelength) was chosen to coincide with the plasmon resonance frequency of Au NPs (absorption peak centered at 532 nm). Proof-of-concept experiments were performed by rapid photothermal conversion, collecting/storing heat energy from a green laser to excite the Au NPs at near their plasmonic resonance wavelength. The laser excited surface plasmons of Au NPs, which transfer resonant energy to lattice vibrations for producing heat

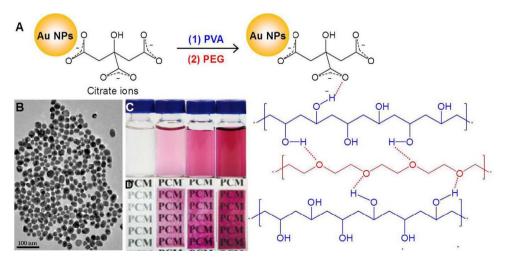


Fig. 1. (A) The simple procedure for fabricating the di-functional nanocomposite film. (B) The TEM image of the Au NPs. (C) Digital photograph of the mixture solutions containing different amounts of Au NPs. Left-to-right: 0, 0.139, 0.406 and 0.677 nM, respectively. (D) Digital photograph of the corresponding nanocomposite films fabricated from the solutions in Fig. 1(C).

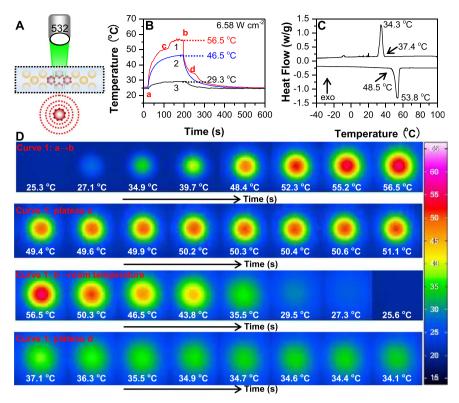


Fig. 2. (A) Schematic illustration of laser excited surface plasmons of Au NPs in the di-functional nanocomposite film. (B) The temperature evolution curves of di-functional nanocomposite film (PEG/PVA/Au NPs, Curve 1), single functional nanocomposite film (PVA/Au NPs, Curve 2) and an unloaded film (PEG/PVA, Curve 3), the power density of the laser is 6.58 W cm⁻². (C) DSC thermal spectra of the di-functional nanocomposite film, in which the solid contents of Au NPs and PEG2000 are 0.23% and 40%, respectively. (D) The time-sequential thermal IR images of the di-functional nanocomposite film.

on a picosecond timescale, was illustrated in Fig. 2A. Fig. 2B shows temperature evolution curves of di-functional nanocomposite film (PEG/PVA/Au NPs, Curve 1), single functional nanocomposite film (PVA/Au NPs, Curve 2) and an unloaded film (PEG/PVA, Curve 3), respectively, under the same power density of 6.58 W cm⁻². In the difunctional nanocomposite film sample, observed in Curve 1 of Fig. 2B. the surface temperature rapidly increased to a plateau at about 56.5 °C and heat storage occurred at near 49 °C which almost consist with phase change start temperature (48.5 °C) of the film-interior PEG in DSC curves (Fig. 2C) during the laser illumination progress. The DSC curves (Fig. S5) for the pure PEG present an endothermic peak centered at 51.0 °C and an exothermic peak centered at 32.7 °C, corresponding to the melting point (T_m) and freezing point (T_f) of the pure PEG. For the di-functional nanocomposite film, we find that the endothermic and exothermic peaks are centered at 53.8 °C and 34.3 °C, respectively, which means that the T_m and T_f of the difunctional nanocomposite film increase significantly relative to those of the pure PEG. Considering PEG is uniformly embedded in PVA networks, the structure change of PEG with temperature change is delayed or in advance, originated from confinement effect of networks to change phase change temperatures of the composites [27,28]. During the cooling process, a temperature plateau can be observed near 35 °C, considering that the stored heat was released from the crystallization of PEG inside the di-functional film interior after switching off the laser. However, the surface temperature in the single functional film sample (Curve 2 in Fig. 2B) can fast increase to a plateau at about 46.5 °C. Meanwhile, in the unloaded film sample (Curve 3 in Fig. 2B), there was negligible change in the surface temperature of sample because the common film could not absorb the green laser. Compared with the di-functional nanocomposite film, no plateau of absorption and release heat obviously appeared in the control samples. By contrast, in the di-functional nanocomposite film, a rapid and effective photothermal conversion and heat storage and

release were observed. In other words, the di-functional nanocomposite film combining rapid photothermal conversion and thermal storage and release had been successfully fabricated by synergetic utilization of plasmonic effect and phase change thermal storage.

Furthermore, the time-sequential thermal IR images of the difunctional nanocomposite film were recorded during the heating ($a\rightarrow b$ in Fig. 2D) and cooling (b→room temperature in Fig. 2D) processes. When a green laser was used to illuminate the di-functional film, the hot zone spread from a spot to a toroid gradually and quickly. The surface temperature was concentric mode distribution, suggesting the Au NPs were equally distributed into PVA thin film matrix without aggregation. With prolonging the illumination time, the local temperature further increased and hot zone was broadened. When the illumination time reached to ~1.5 min, the inflection point occurred at temperature of 49 °C, consistent with the phase change temperature of the film-interior PEG. The IR images of plateau c were nearly uniform during the phase transition progress. Prolonging the illumination time to ~2.5 min, the terminal balance temperature remained unchanged at 56.5 °C during the rest of illumination time. On the contrary, when the laser was closed and the sample was left to cool down naturally, hot zone gradually diminished, remains the same (plateau d of Fig. 2D) and disappeared finally. The shape of all films remained near unchanged after illumination, showing that the films kept stable without leakage of PEG. The series of IR images vividly demonstrate that rapid photothermal conversion and heat storage and release processes proceed via an instant and intense plasmonic heat generation when illuminated with a low-power laser. Meanwhile, these di-functional nanocomposite films can also be utilized as thermal energy storage materials for exterior protective films placed over soil, wrapped around fodder or covered over greenhouses, which would absorb heat from the surrounding air and solar radiation during daytime, releasing stored heat back into the room overnight subsequently.

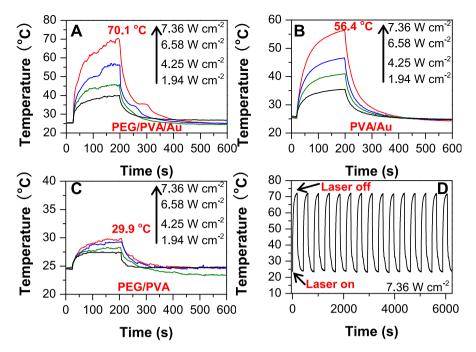


Fig. 3. The temperature evolution curves of (A) the di-functional nanocomposite film (PEG/PVA/Au NPs), (B) single functional nanocomposite film (PVA/Au NPs) and (C) an unloaded film (PEG/PVA) under 1.94, 4.25, 6.58 and 7.36 W cm⁻² of laser power intensity illumination conditions, respectively. (D) The temperature to time curves of the di-functional nanocomposite film over 15 cycles under 7. 36 W cm⁻² of laser power intensity illumination conditions.

The input laser energy played an important role to adjust the temperature of illuminated samples, in that the temperature was determined by the dynamic equilibrium among input laser energy, heat collection and dissipation [29]. Based on the approach of Pustovalov [30], the temperature of a spherical Au NP by a power density of I_0 at steady state can be described to be $T_{o}=T_{\infty}+I_{o}K_{abs}r_{o}/4k_{\infty}$ (1), where K_{abs} is the absorption efficiency factor, r_0 is the radius of a particle, T_{∞} is the macroscopic balance temperature, and k_{∞} is the coefficient of thermal conductivity of the surrounding medium. Therefore, based on Eq. (1), the temperature of samples will increase with increasing input laser power. In the difunctional nanocomposite film, Fig. 3A showed that the maximum temperature profile of di-functional film rapidly reached a higher plateau than all other film samples. For example, under the same laser power illumination (such as 7.36 W cm⁻²), the temperatures of the difunctional, single functional, and unloaded film could reach to 70.1 °C (Fig. 3A), 56.4 °C (Fig. 3B), and 29.9 °C (Fig. 3C) within ~200 s, respectively. The thermal storage efficiency of each film was calculated in Table S1 (Supplementary Materials), and the thermal storage efficiency of the PEG/PVA/Au NPs film was increased ultimately by 201% comparing to PVA/Au NPs under the laser illumination power density of 6.58 W cm⁻². As a result, all the Au NPs loaded plasmonic nanocomposite films have higher temperature values than the unloaded film sample. The difference could be understood from the comparison of the maximum temperature profile in all the films under the same laser illumination. The Au NPs filled films can convert the incident laser light into thermal energy to heat the whole film system. The higher heating temperature implies quicker photothermal conversion ability, which clearly demonstrates the advantage of plamonic nanostructures. Besides, the filled concentration of Au NPs also affected the photothermal conversion behavior. The higher filled concentration of Au NPs, the higher heating temperature could be obtained. A low loading concentration of Au NPs in current films would be important and attractive for large scale production and applications considering the cost reduction. What's more, the durability of the difunctional nanocomposite films has also been examined. The temperature to time curve (Fig. 3D) reveals a high cycling behavior and welldefined response kinetics of the photothermal conversion process, indicating a stable performance over 15 cycles under high laser power intensity illumination condition (7.36 W cm⁻²).

2.3. Solar-to-heat conversion

Besides a low-power focused laser that can be converted and stored as illuminate in our di-functional films, solar radiation can also be applied to drive the energy conversion and storage in di-functional films. Under simulated solar illumination (Fig. 4A) at the same environmental conditions, the surface temperature of the di-functional film would quickly increase to about 90 °C (Fig. 4B). Nevertheless, the surface temperature of the ordinary and unloaded PVA film only reaches to about 60 °C (Fig. 4B) in a slowly increasing temperature tendency. Following the cooling down after turning off the sunlight, the stored heat was released from the di-functional film during the crystallization of PEG, appearing a time delay and a longer plateau of steady-state temperature (~30 °C) and time delay than that of unloaded film (Fig. 4B), apparently. The thermal storage efficiency of the PEG/PVA/Au NPs film was increased ultimately by 148% comparing to PVA film under the same sunlight illumination. Undoubtedly, the

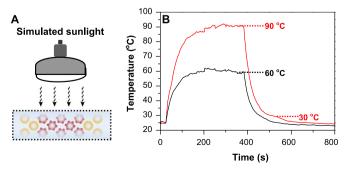


Fig. 4. (A) Illustration of the simulated solar illumination experiment. (B) The temperature evolution curves of the di-functional nanocomposite film (PEG/PVA/Au NPs) (red line) and an unloaded PVA film (black line) under the illumination of a simulated sunlight.

above results have shown that the obtained di-functional films have the excellent ability to effectively and rapidly convert and store solar energy as thermal energy.

3. Conclusions

In conclusion, the di-functional nanocomposite films with the ability to effectively and rapidly convert and store solar energy as thermal energy had been successfully fabricated. The as-prepared difunctional nanocomposite films show the rapid and uniform heating ability by plasmonic heat produced via equally dispersed Au NPs at a low concentration under sunlight or low power laser intensity. Simultaneously, the thermal storage and release capacity can also be realized by film-interior reversible phase transformation of PEG molecules. The thermal storage efficiency of the di-functional nanocomposite film was enhanced by 201% comparing to single functional nanocomposite even if the laser power density was 6.58 W cm⁻². The durability of the di-functional nanocomposite films has also been examined, indicating a stable performance over 15 cycles under a high laser power intensity illumination condition. Our di-functional nanocomposite films will have wide application fields related to energy conversion and storage.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2017.02.017.

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