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Synergfistfic photothermafl-thermoeflectrfic-photovofltafic energy generatfion vfia a transparent spectrafl moduflatfing soflar modufle

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A B S T R A C T

The effficfiencfies of photovofltafic (PV) and thermoeflectrfic (TE) have been flfimfited by the fintrfinsfic materfiafls propertfies. In soflar appflficatfions, PV utfiflfizes the shorter waveflength end of the soflar spectrum whfifle fits flonger portfion (IR) can be photothermaflfly (PT) converted to heat by specfiafl nano structures for TE eflectrficfity generatfion. We have devefloped spectrafl moduflatfing nano systems made of Fe_3O_4@$Cu_{2-X}S$ nanopartficfles and chflorophyflflfin capabfle of synergfistfic PT-TE-PV soflar harvestfing and energy generatfion. In thfis system, soflar flfight fis harvested through the transparent photothermafl spectrafl moduflator (TPSM) and segregated finto dfifferent waveflengths: the IR fis absorbed to photothermaflfly heat up the TE hot end for the requfired thermoeflectrfic temperature span; the UV/vfisfibfle fis dfirected to PV wfith reduced IR for sfignfifficantfly reduced heatfing, thus enhanced power conversfion effficfiency (PCE). Upon removafl of IR, the PV surface temperature can be flowered from 86.9 ℃ to 65 ℃ after 120 mfin soflar firradfiatfion, resufltfing fin PCE fincrease from 16.3 % (dropped from 25.1 % at 0 mfin) to 19. 4 %. A PT – TE – PV soflar energy modufle (PTPSEM) fis desfigned based on TPSM to synergfistficaflfly generate energy by separatefly utfiflfizfing the fuflfl spectrum of soflar flfight. Usfing the same soflar flfight source, whfifle generatfing eflectrficfity vfia PV, an addfitfionafl 2.4 % fis gafined by a serfies of commercfiafl thermoeflectrfic generators (TEG), addfing up to a totafl of 21. 8 % system effficfiency whfich sfignfifficantfly exceeds the average effficfiency of the commercfiafl sfiflficon PV panefl used fin thfis study. The spectrafl moduflatfion mechanfism through TPSM fis fidentfiffied based on the optficafl behavfiors of chflorophyflflfin and Fe_3O_4@$Cu_{2-X}S$. Aflso dfiscussed fis the desfign concept of PTPSEM.

1. Introduction

The power conversfion effficfiencfies of PV and TE have been flfimfited by the fintrfinsfic propertfies; respectfivefly, ~ 25 % for PV and ~ 5–8 % for TE. The processes drfivfing most photovofltafics utfiflfize soflar energy at waveflengths beflow about 1000 nm fin the UV/Vfis – NIR range of the soflar spectrum. About 58 percent of the energy densfity of the soflar spectrum flfies fin thfis waveflength range wfith the other 42 percent occurrfing at flonger waveflengths. Conventfionafl soflar ceflfls typficaflfly have substantfiafl absorptfion fin the sub – band – gap waveflength range above approxfimatefly 1000 nm [1]. Thfis absorbed flong waveflength soflar energy contrfibutes to heatfing of the PV panefls resufltfing fin sfignfifficant effficfiency decrease wfith temperature [2]. A typficafl temperature coeffficfient for PV output power fis – 0.5 percent per ℃ [3]. A standard PV modufle, absorbfing IR aflong wfith UV and vfisfibfle soflar radfiatfion can operate 20 to 40 °C above ambfient temperature fleadfing to effficfiency flosses of up to 20 % [2–3]. Numerous researchers have finvestfigated actfive cooflfing of PV modufles to fimprove effficfiency [4–7]. However actfive cooflfing fincreases system compflexfity and fimposes energy costs for actfive eflements such as pumps and fans.

The potentfiafl of combfing PV and a thermoeflectrfic generator (TEG) has been prevfiousfly expflored [8–9]. In many cases the thermoeflectrfic modufle fis attached dfirectfly to the PV panefl. Heat generated by PV fin the IR band fis converted to eflectrficafl energy by the thermoeflectrfic. Thfis approach suffers from the compfletefly dfifferent temperature dependence of PV and thermoeflectrfic effficfiencfies. Thermoeflectrfic devfice output fincreases wfith temperature whfifle PV output decreases wfith temperature. Thus combfined PV and thermoeflectrfic devfices have an finherent drawback due to finverse temperature dependence.

Aflthough the photothermafl (PT) effects of nanopartficfles have been extensfivefly studfied for medficafl therapy [10–19],a few studfies on the transparent photothermafl thfin ffiflms and buflk materfiafls have been reported for energy appflficatfions. We have recentfly devefloped transparent, spectrafl seflectfive, and photothermafl thfin ffiflms based on porphyrfins and firon oxfides [20–26], capabfle of rafisfing temperature up to 76 °C under sfimuflated soflar flfight [22]. The optficafl absorptfions of the hybrfid ffiflms are spectraflfly tuned wfith strong absorptfions fin the UV and IR regfions but kept fin mfinfimum fin the vfisfibfle band for hfigh average vfisfibfle transmfittance. In thfis fashfion, the soflar flfight can be harvested through mufltfipfle flayers and converted to thermafl energy fin a 3D cubofid. The thermafl energy generated fin a conffined voflume can be utfiflfized to produce eflectrficfity vfia thermoeflectrfic devfices for a varfiety of appflficatfions.

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Furthermore, the transparent hybrfids can be spectraflly tuned to seflectfivefly absorb soflar flfight fin the desfignated frequencfies, such as UV and IR as a photonficaflfly optfimfized flfight source for PV appflficatfions.

In thfis study, we report on the deveflopment of the transparent photothermafl spectrafl moduflator (TPSM) that fis engfineered for mufltfipfle functfions: (1) sfince the TPSM fis transparent, the sfimuflated soflar flfight can pass through fit as the flfight source for a commercfiafl sfiflficon PV panefl; (2) meanwhfifle, the soflar flfight (mafinfly IR) fis absorbed by TPSM and converted to thermafl energy vfia the photothermafl effect; (3) the thermafl heat fis utfiflfized for TEGs to produce eflectrficfity through mufltfipfle surfaces, and (4) the TPSM can spectrafl seflectfivefly remove the IR portfion for reducfing PV surface heatfing resufltfing fin enhanced photon conversfion effficfiency (PCE). In thfis fashfion, we combfine the PT, TE, and PV effects for synergfistficaflfly producfing thermafl and eflectrficafl energfies by unfique materfiafls desfign of TPSM.

The concept of PT ϒ TE ϒ PV moduflefis schematficaflfly fiflflustrated fin Ffig. 1. As shown fin thfis ffigure, the TPSM fis structuraflfly tafiflored to specfified absorptfions from UV to IR for the most effficfient 3D soflar harvestfing and energy generatfion. As the soflar flfight fis harvested by the transparent nano hybrfids, most of the IR fis absorbed (~42 %) and photothermaflfly (PT) actfivated to heat up the hot end of TE (ffigure of merfit of TE fis proportfionafl to temperature span). The UV/Vfis portfion (~58%) can pass through the TPSM for PV eflectrficfity generatfion. In thfis fashfion, the entfire spectrum of soflar flfight fis fuflfly utfiflfized for energy generatfion vfia combfined effects of PV, PT, and TE. The spectrafl tunabfiflfity of the TPSM flfies on structurafl desfigns for spectrafl moduflated absorptfions. Further, TPSM can be rendered transparent enabflfing whfite flfight passfing through mufltfiflayers, prfismatfic soflfids, or a cube, therefore, transformfing soflar harvestfing from 2D to 3D wfith sfignfifficantfly fincreased energy densfity.

We devefloped a unfique TPSM contafinfing efither $Fe_3O_4@Cu_{2-X}S$ nanopartficfles or chflorophyflflfin whfich fis hfighfly transparent, spectrafl seflectfive, strongfly photothermafl, and capabfle of absorbfing and convertfing desfignated photon energfies for the most effficfient energy generatfion vfia the PT, TE, and PV effects. Varfious PT – TE – PV soflar energy moduFles (PTPSEM) were desfigned based on TPSM as shown fin Ffig. 2. The basfic desfign concept fis depficted fin Ffig. 2a. As shown fin thfis ffigure, the sfimuflated soflar flfight passes through transparent TPSM for two purposes: 1) Photothermaflfly generatfing thermafl energy for heatfing up the hot end of the thermoeflectrfic generator (TEG). Due to the temperature dfifference between the hot and cofld ends of TEG, eflectrficfity fis generated mafinfly by utfiflfizfing the IR portfion of the soflar flfight. 2) Sfince TPSM fis transparent, sfimuflated soflar flfight can pass through fit, reachfing the PV panefl beflow for eflectrficfity generatfion. In thfis fashfion, the same soflar flfight source can be spectraflfly utfiflfized to produce eflectrficfity sfimufltaneousfly by TE and PV through PT. Furthermore, the IR portfion fis absorbed by TPSM (converted to heat for TEG), resufltfing fin reduced heatfing on the PV panefl surface.

Based on the concept depficted fin Ffig. 2a, we desfigned dfifferent PTPSEMs for optfimfized soflar harvestfing and energy generatfion (both thermafl and eflectrficafl energy). Consfiderfing flfight power attenuatfion through the TPSM due to fits thfickness (Ffig. 2a), we desfigned a 5-sfided box made of TPSM wfith a cfircuflar openfing on the top sfide. As shown fin Ffig. 2b, the center beam of the sfimuflated soflar flfight can dfirectfly reach the commercfiafl sfiflficon PV panefl (Ffig. 2c) through the top cfircfle openfing for generatfing eflectrficfity wfith the specfified PV PCE. However, the rfim of flfight fin fact passes the 2 mm thfick top cover (Ffig. 2b) wfith portfion of IR removed to reduce the PV surface heatfing (the so-caflfled spectrafl moduflatfion). Meanwhfifle, the 4-sfide waflfls of TPSM are photothermaflfly actfivated to heat up the hot ends of 4 PTGs for generatfing eflectrficfity (Ffig. 2d).

The overaflfl structure of PTPSEM fis schematficaflfly fiflflustrated fin Ffig. 2d. It can be seen fin thfis ffigure that the soflar flfight fis spectraflfly utfiflfized vfia TPSM for effficfient energy harvestfing and generatfion. The TPSM fis composed of efither $Fe_3O_4@Cu_{2-X}S$ or chflorophyflflfin, both are strongfly photothermafl and spectrafl seflectfive wfith unfique optficafl characterfistfics. The PTPSEM can synergfistficaflfly generate energy through the photothermafl, thermoeflectrfic, and photovofltafic effects accordfing to spectraflfly moduflated photon frequencfies: IR fis absorbed by TPSM to heat up TEGs; removafl of IR from soflar flfight reduces PV panefl heatfing for enhanced PCE, and the same flfight source wfith most of UV – Vfis (IR removed) fis utfiflfized for PV.

2. Experimental details

2.1. Materfiafls synthesfis

The foflflowfing chemficafls were used fin thfis research: firon (III) acetyflacetonate ($Fe(acac)_3$, ≥99.9%), copper (II) acetyflacetonate ($Cu(acac)_2$, ≥99.9%), ofleyflamfine (70%), suflfur (99.998%), N – methyfl – 2 – pyrroflfidone (NMP, 99.5%), chfloroform (≥99.9%), tetrahydrofuran (THF, 99.9%), fisopropyfl aflcohofl (IPA, 99.7%), and poflyethyflene gflycofl (PEG); afflfl were purchased from Sfigma – Afldrfich Inc. Cycflohexane (99.5%) was purchased from Tedfia Inc.

$Fe_3O_4@Cu_{2-X}S$ nanopartficfles were synthesfized by foflflowfing a prevfious report[23]. A certafin amount of ofleyflamfine was heated to 300 °C fin nfitrogen gas envfironment for a perfiod. Meanwhfifle, amount of $Fe(acac)_3$ was dfissoflved fin the NMP/ofleyflamfine soflutfion (4:3,v/v) whfich was added finto a preheated ofleyflamfine to form Mfixture A. The Mfixture A was stfirred for 10 mfin at 300 °C and then coofled down to 70 °C for 10

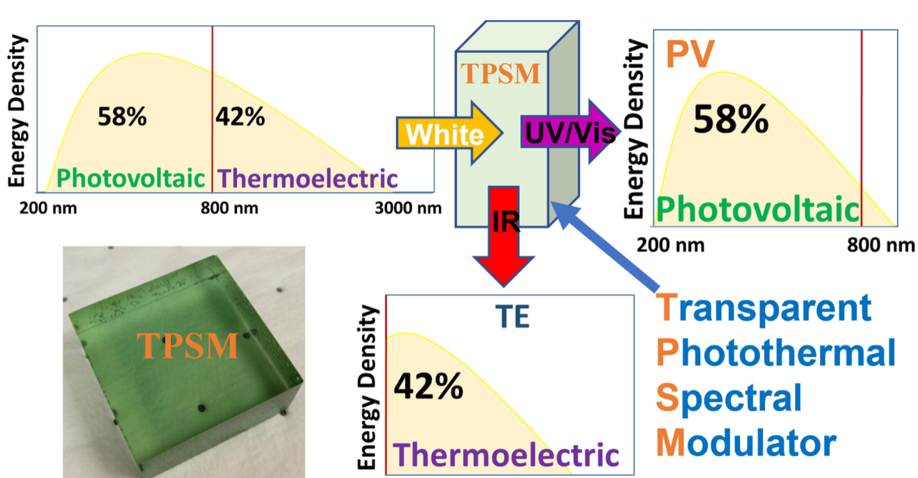

Fig. 1. Schematfic dfiagram showfing the spectrafl tunabfle nano hybrfid as a waveflength segregator and PT heater.

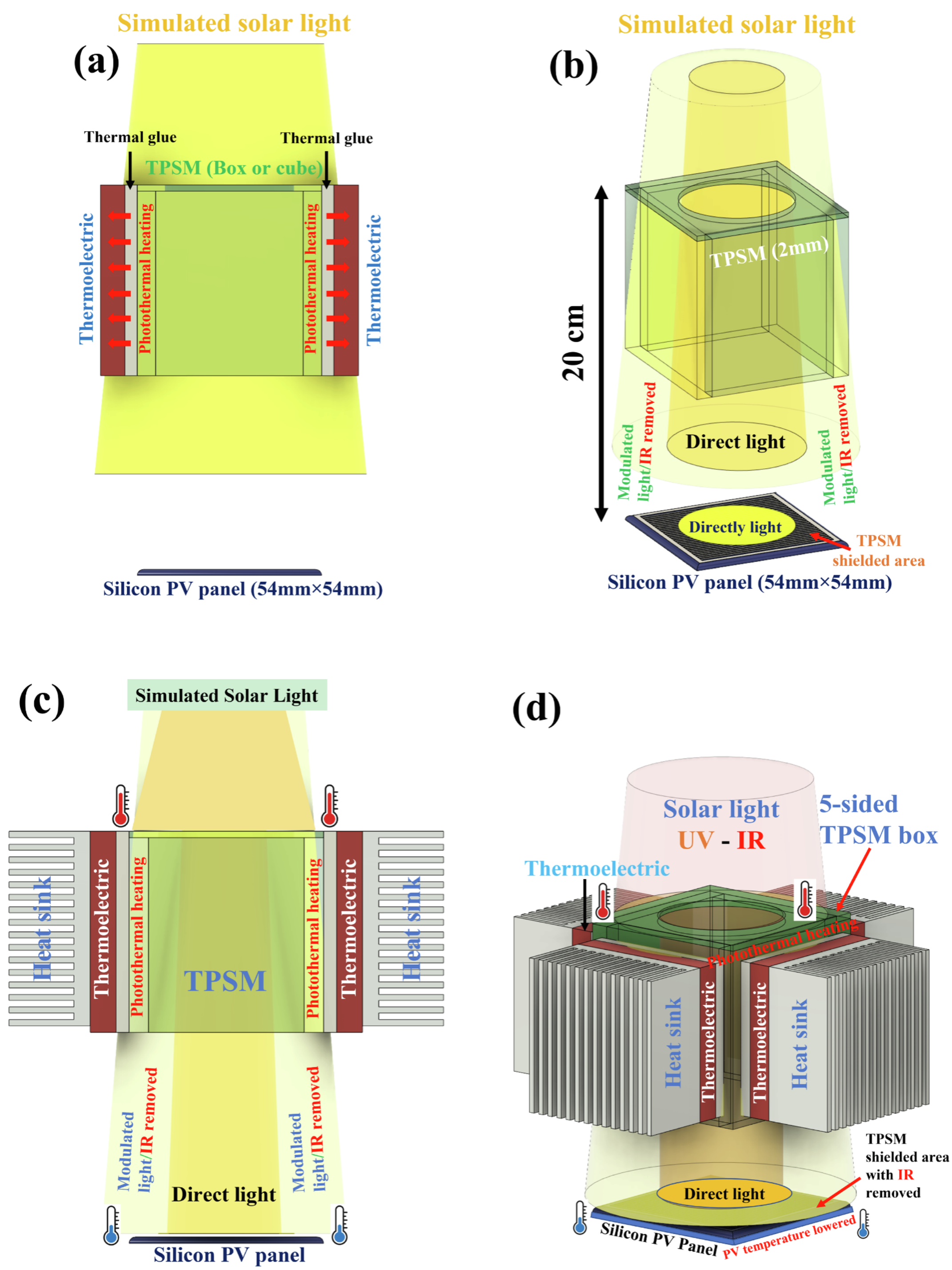

Fig. 2. Schematfic dfiagrams showfing (a) the basfic concept of PT – TE – PV soflar energy modufle (PTPSEM) consfistfing of a transparent photothermafl spectrafl moduflator (TPSM), the thermoeflectrfic generators (TEG) on the sfide waflfls of TPSM, and a commercfiafl sfiflficon PV panefl at the bottom whfich can recefive soflar flfight that fis spectraflfly moduflated by transparent TPSM. The sfimuflated flfight ffirst passes the TPSM, generatfing heat that fis transferred to TEGs, then shfines on the PV panefl; both TEG and PV synergfistfica flfly generate eflectrfickity vfia utfiflfizfing fuflfl soflar spectrum. (b) To enhance flfight fintensfity on the PV surface, a 5-sfided box fis made of TPSM wfith waflfl thfickness of 2 mm. A cfircuflar openfing on the top waflfl fis to flet soflar flfight dfirectfly reach PV wfith hfigh photon fintensfitfies. (c) The rfim of flfight wfiflfl pass through the 2 mm thfink TPSM waflfl on the top to remove portfion of IR for reducfing PV surface heatfing. (d) 3D overvfiew of the PTPSEM wfith four TEGs on the sfide waflfls of the 5-sfided TPSM box and a commercfiafl PV panefl at the bottom, recefivfing the fuflfl spectrum of the soflar flfight fin a spectrafl seflectfive fashfion.

mfin. Amount of suflfur was dfissoflved fin a ofleyflamfine/cycflohexane mfixture (6:5,v/v) to form Mfixture B. Mfixture B was sflowfly finjected finto Mfixture A to form Mfixture C at 70 °C and stfirred for 10 mfin. Cu (acac)$_2$ was dfissoflved fin the ofleyflamfine/chfloroform mfixture (1:4,v/v) to form Mfixture D whfich fis made of Cu (acac)$_2$ fin ofleyflamfine/cycflohexane mfixture (6:5,v/v). Mfixture D was then finjected finto Mfixture C. After stfirrfing at 70 °C for 30 mfin, the $Fe_3O_4@Cu_{2-X}S$ nanopartficfles were obtafined. The $Fe_3O_4@Cu_{2-X}S$ nanopartficfles were coflflected by a strong magnet. The coflflected nanopartficfles were washed wfith methanofl and then drfied by oven under vacuum. Ffinaflfly, $Fe_3O_4@Cu_{2-X}S$ nanopartficfles were dfispersed fin THF for flater use.

Epoxy resfin and sfiflficon mofld were used to deveflop TPSM wfith varfious geometrfies. $Fe_3O_4@Cu_{2-X}S$ and chflorophyflflfin wfith dfifferent ratfios and concentratfions were dfispersed fin epoxy resfin and weflfl mfixed to ensure homogenefity. The mfixed soflutfion was then poured finto a sfiflficon mofld and cured for 24 h. The concentratfions of the buflk sampfles were controflfled at 200 μg/cm³. Fig. 3 shows the photographs of cubfic TPSM made of chflorophyflflfin (Fig. 3a) and Fe_3O_4@$Cu_{2-X}S$ (Ffig. 3b). As shown fin thfis ffigure, the bulk TPSMs of both chflorophyflflfin and Fe_3O_4@$Cu_{2-X}S$ appear to be transparent and homogeneous wfith respectfive flfight green (Ffig. 3a) and amber (Ffig. 3b) coflors. Soflar flfight can pass through fit dependfing on the transparency and thfickness. Usfing Fe_3O_4@$Cu_{2-X}S$ or chflorophyflflfin, the TPSM was made finto 5-sfided boxes as shown fin Fig. 2b. As noted above, the concentratfion of Fe_3O_4@$Cu_{2-X}S$ or chflorophyflflfin fin the TPSM box was controflfled at 200 μg/cm³.

2.2. Materfials characterfizatfion

The TPSM sampfles were characterfized for fuflfl-spectrum absorptfion and transmfittance. Mafintafinfing hfigh AVT fis crfitficafl to ensure sfignfifficant flfight power densfity on the PV cefll surface. In thfis study, we focused on characterfizatfion of the porphyrfin compounds and firon oxfides, namefly, chflorophyflflfin and Fe_3O_4@$Cu_{2-X}S$. These compounds exhfibfit unfique absorptfion characterfistfics provfidfing a versatfifle optficafl base for makfing TPSMs fin a wfide range of photon frequency. To observe thefir fintrfinsfic optficafl behavfiors, the absorptfion and transmfittance spectra were obtafined from the soflutfions of these compounds to avofid the buflk effects. Fig. 4 shows the absorptfion spectra of chflorophyflflfin and Fe_3O_4@$Cu_{2-X}S$. The concentratfions of chflorophyflflfin and chflorophyflflfin were both ffixed at 0.01 mg/mfl.

As shown fin Ffig. 4a, chflorophyflflfin has an fintensfive absorptfion peak at 404 nm and a smafll one at 630 nm formfing a so-caflfled "saddfle-flfike" spectrum. Thfis fis the typficafl absorptfion characterfistfic of the porphyrfin compound whfich fis partficuflarfly usefufl for spectrafl seflectfive soflar harvestfing and generatfing photothermafl energy, whfifle remafinfing hfigh AVT. As shown fin Ffig. 4a, the strong peaks at 404 nm and 630 nm findficate consfiderabfle absorptfions fin the UV and NIR regfions for conversfion of photons to thermafl energfies. Low absorptfions fin the vfisfibfle regfion render the porphyrfin hfighfly transparent for makfing TPSM (Ffig. 3) fin the PT – TE – PV soflar energy modufle (Ffig. 2).

The Fe_3O_4@$Cu_{2-X}S$ nanopartficfles are known for thefir IR absorptfions. Ffig. 4b shows the absorptfion spectra of both Fe_3O_4 and Fe_3O_4@$Cu_{2-X}S$ nanopartficfles fin soflutfions for comparfison. As shown fin thfis ffigure, Fe_3O_4 typficaflfly exhfibfits a strong absorptfion fin the UV regfion and qufite rapfidfly subsfides over the vfisfibfle and IR regfions. By coatfing a thfin flayer of $Cu_{2-X}S$ on the Fe_3O_4 nanopartficfles, the Fe_3O_4@$Cu_{2-X}S$ soflutfion exhfibfits a broad absorptfion peak extendfing to 1400 nm. Thfis strong IR absorptfion can be used to reduce the PV surface heatfing from the soflar flfight. The IR

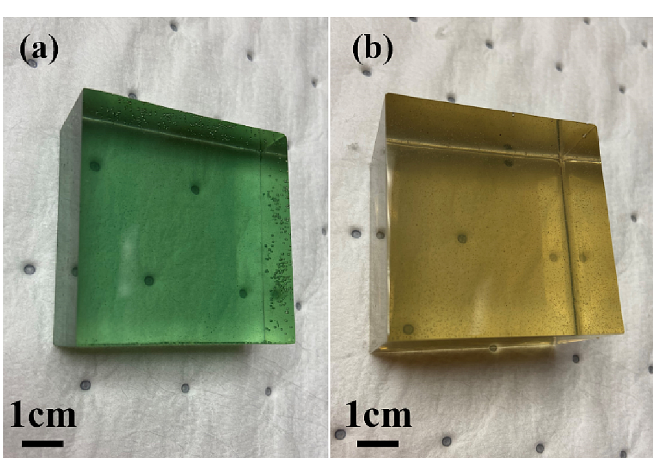

Fig. 3. Photograph of a transparent photothermafl spectrafl moduflator (TPSM) wfith (a) chflorophyflflfin and (b) Fe_3O_4@$Cu_{2-X}S$ nanopartficfles fin epoxy resfin. The concentratfion of Fe_3O_4@$Cu_{2-X}S$ or chflorophyflflfin fin the TPSM box was controflfled at 200 μg/cm³.

absorptfion of Fe_3O_4@$Cu_{2-X}S$ has been attrfibuted to the flocaflfized surface pflasmon resonance (LSPR) of $Cu_{2-X}S$ fin the IR regfion [27]. The TPSM made wfith the Fe_3O_4@$Cu_{2-X}S$ nanopartficfles can spectraflfly moduflate the soflar flfight by absorbfing most of IR whfich contrfibutes to PV surface heatfing.

2.3. Photothermal, Thermoelectrfic, and photovoltafic characterfizatfion experfimental detafils

An AOSHIKE Mficro Soflar Cefll wfith 54 mm × 54 mm (bought from amazon) was used fin thfis study. The measurement setup for I – V characterfizatfion fis schematficaflfly shown fin Ffig. 5a. A soflar sfimuflator (Newport) was used as a flfight source for a duratfion of 120 mfin for each experfiment so that the heatfing effect was recorded. The soflar cefll surface temperature was monfitored by usfing a thermafl camera (FLIR, Inc.). The I – V curve measurement was performed by usfing Kefithfley 2400 finstrument. Afideepen thermoeflectrfic generators (sfize: 40 mm × 40 mm × 3.6 mm wfith Bi_2Se_3 as thermoeflectrfic eflements, bought from amazon) were used to convert heat generated by the 5-sfided TPSM box (Ffig. 2d) finto eflectrficfity. TEGs were attached onto the 4 sfide surfaces of the TPSM box (Ffig. 2d) after 120 mfin heatfing. ΔT was caflcuflated by usfing the temperature dfifference between the hot and cofld ends of TGE whfich was measured by thermafl coupfles.

The effficfiency of soflar cefll can be caflcuflated usfing the foflflowfing equatfion:

$$\eta_{PV} = \frac{P_{out}}{P_{in}} = \frac{I_{SC}V_{OC}FF}{P_{in}} \quad (1)$$

where P_{out} fis output power, P_{in} fis output power, I_{SC} fis short – cfircufit current, V_{OC} fis open – cfircufit Vofltage, I_{MP} fis current densfity at maxfimum power, V_{MP} fis vofltage at maxfimum power, P_{max} fis the maxfimum output power, and FF fis ffiflfl factor. It shoufld be noted that P_{in} used to determfine PCE fis the flfight power densfity on the PV panefl wfithout passfing through the TPSM (Ffig. 2). Due to varfied flfight transmfittances of the TPSM, the flfight power densfity on the PV surface aflso varfies.

The thermoeflectrfic measurement setup fis schematficaflfly shown fin Ffig. 5b. The effficfiency of thermoeflectrfic generator fis caflcuflated by

$$\eta = \frac{P_{TE}}{Q_{in}} \quad (2)$$

where P_{TE} (W) fis power of TE generator, Q_{in}(J) fis the power finput of the soflar sfimuflator.

P_{TE} fis caflcuflated based on the output on a 10 Ω resfistor, the current I (amp), and vofltage V (voflt) of the cfircufit (Ffig. 5b). The output of TEG can be wrfitten as:

$$P_{TE} = I \times V \quad (3)$$

Seebeck coeffficfient of the combfined TEGs can be caflcuflated as:

$$S = \frac{E}{\Delta T} = -\frac{V}{T_H - T_C} \quad (4)$$

where E fis the vofltage generated and ΔT fis the temperature dfifference between the hot and cofld ends of the TEG.

Ffigure of merfit (ZT) can be caflcuflaated by the expressfion:

$$ZT = \frac{S^2\sigma}{\kappa}T \quad (5)$$

where κ fis thermafl conductfivfity of TEG, σ fis eflectrficafl conductfivfity, and T fis the absoflute temperature.

Power Factor (PF):

$$PF = S^2\sigma \quad (6)$$

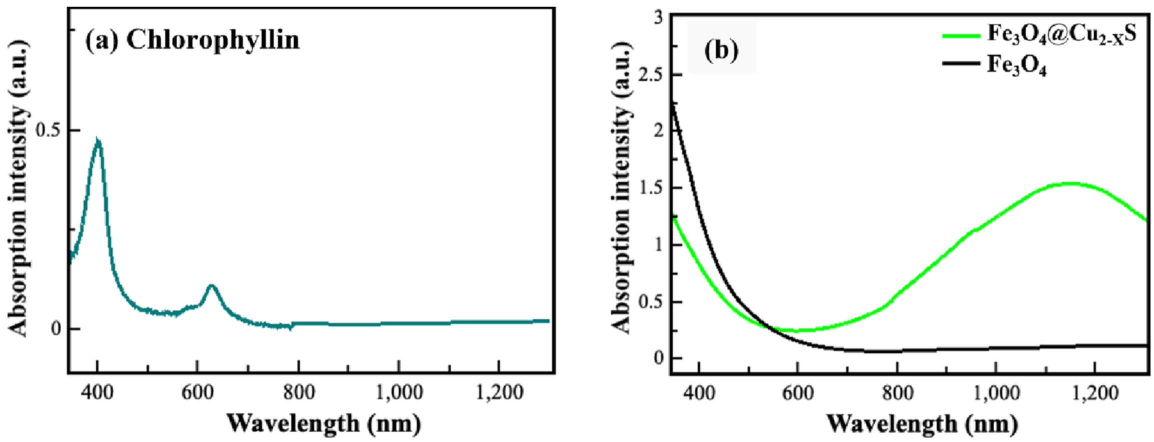

Fig. 4. Absorption spectra of (a) chlorophyllin, and (b) Fe_3O_4 and $Fe_3O_4@Cu_{2-X}S$.

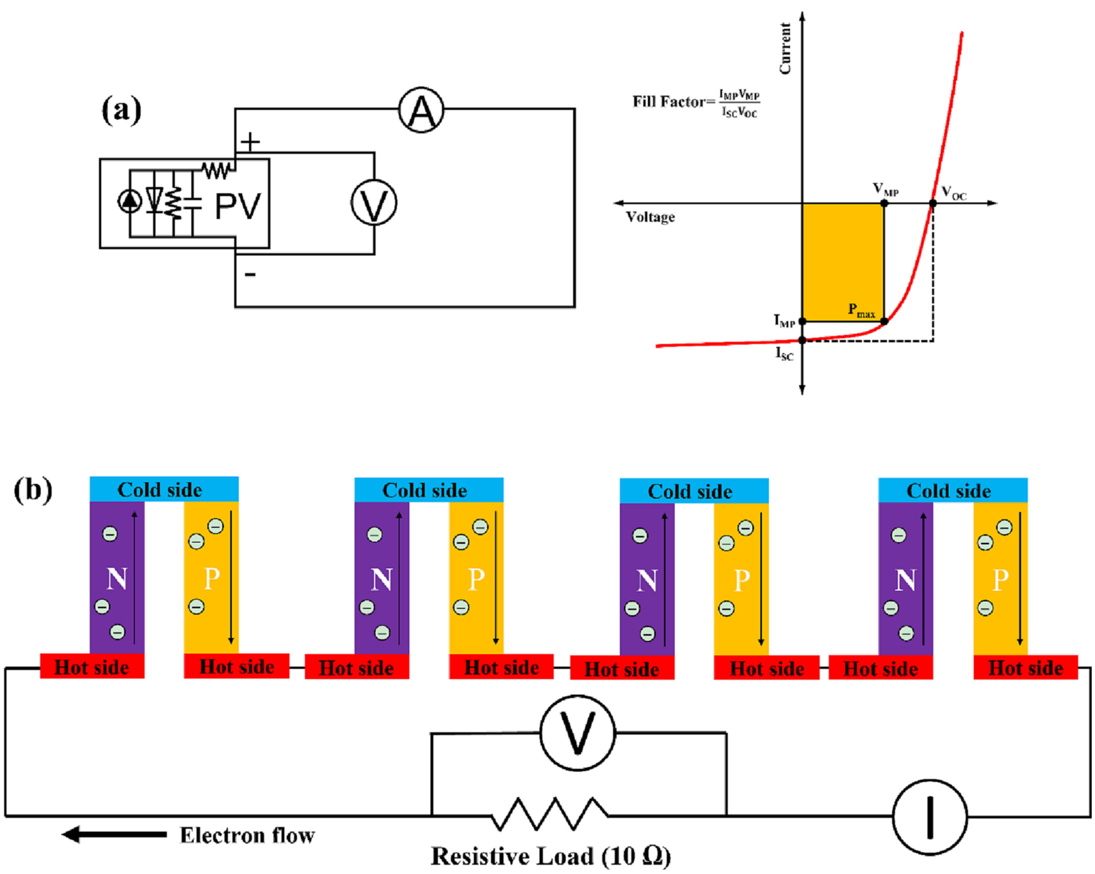

Fig. 5. Schematic diagrams showing (a) I – V curve measurement set up, (b) TEG measurement set up.

2.4. Charaterzation of the TPSM cube with $Fe_3O_4@Cu_{2-X}S$ and chlorophyllin

Fig. 6a shows the PTPSEM experimental set up with four commercial TEGs on the four faces of a TPSM cube (dimensions: 5 cm × 5 cm × 5 cm). The TPSM cube is composed of $Fe_3O_4@Cu_{2-X}S$ or chlorophyllin dispersed in the matrix of epoxy resin with a concentration of 0.01 mg/ml. Upon simulated solar light irradiation (1.58 W), the TPSM is photothermally activated to convert incoming photons to thermal energy. As shown in Fig. 6b, the highest temperatures of the side walls can reach 66.6 ℃ and 64.9 ℃, respectively for the $Fe_3O_4@Cu_{2-X}S$ and chlorophyllin TPSM cube. As shown in this figure, due to the photothermal effects of $Fe_3O_4@Cu_{2-X}S$ and chlorophyllin in the TPSM cubes, the temperatures rise quite rapidly upon solar light irradiation (1.58 W). The solar light is turned off at 120 min; therefore, the temperatures start to drop off thereafter. With these significant temperatures, the four TEGs on the 4 – side walls of TPSM cube generated TE voltages of 1.864 V and 1.845 V (Fig. 6c), and TE powers of 0.189 W and 0.187 W (Fig. 6d), respectively, for $Fe_3O_4@Cu_{2-X}S$ and chlorophyllin TPSM cubes. However, due to heat transfer between the hot and cold ends of TEGs, the temperature differences, ΔT, are reducing from above 43.6 ℃ to 16.8 ℃ as shown in Fig. 6e. Consequently, both voltages and powers are also reduced. Notice that the drops in voltage and power become much less rapid after 3 min (Fig. 6c and 6d). The TE efficiencies with 4 TEGs are 11.9% and 11.8% respectively for the $Fe_3O_4@Cu_{2-X}S$ and chlorophyllin TPSM cubes when ΔT is at the maximum as shown in Fig. 6f.

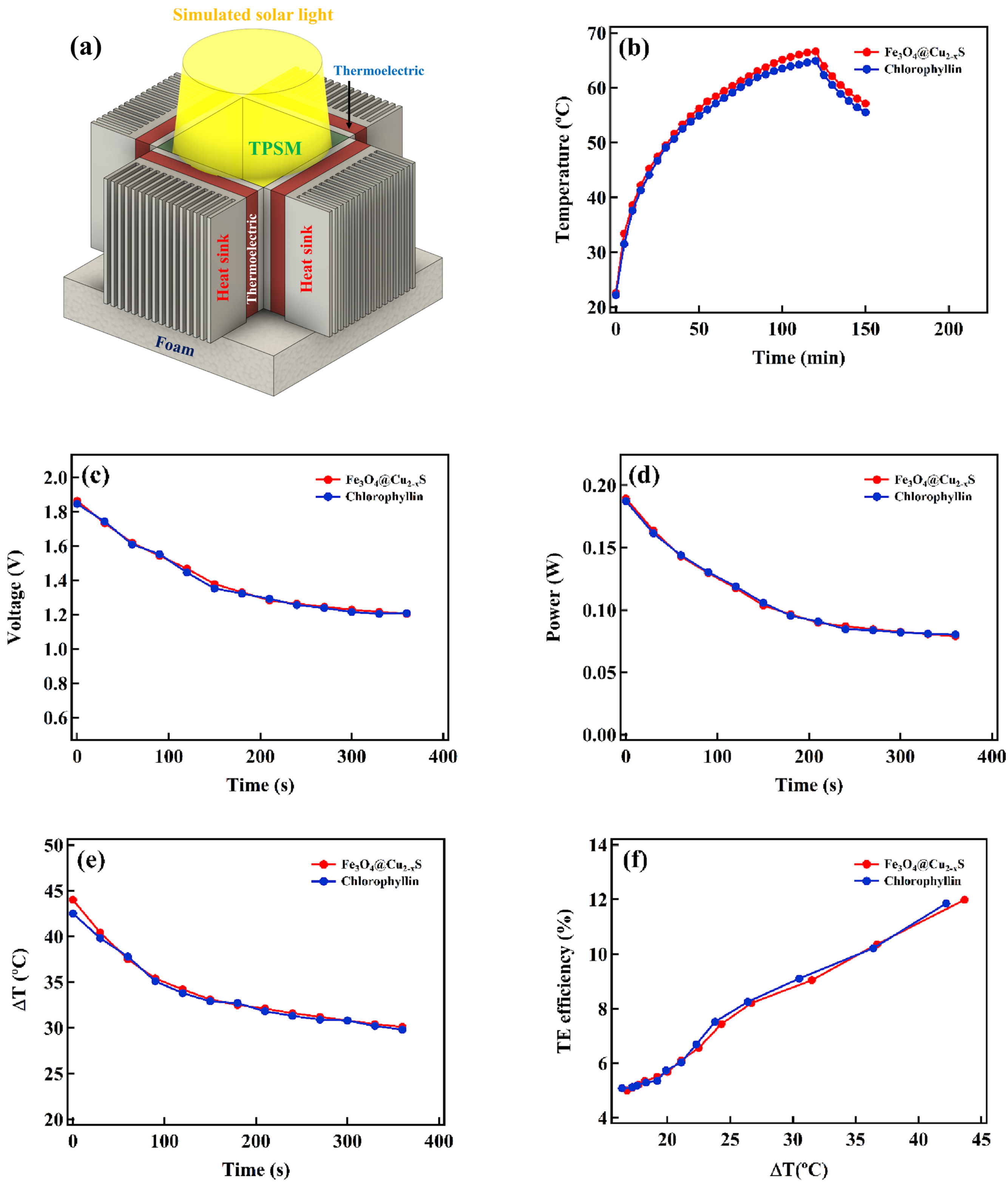

Fig. 6. (a) Schematfic dfiagram showfing the PTPSEM experfimentafl set up wfith four commercfiafl TEGs on the four faces of the TPSM cube. (b) The cube sfide waflfl surface temperature vs tfime (heatfing cruves) for the TPSM wfith $Fe_3O_4@Cu_{2\text{-}x}S$ or chflorophyflflfin dfispersed fin the epoxy resfin matrfices (Ffig. 3); (c) The TE vofltages generated by TEGs on the 4-sfide waflfls of the TPSM cube (fin serfies) wfith $Fe_3O_4@Cu_{2\text{-}x}S$ or chflorophyflflfin dfispersed fin the epoxy resfin matrfix (Ffig. 3); (d) TE power outputs generated by TEGs on 4-sfide waflfls of the TPSM cube (fin serfies) wfith $Fe_3O_4@Cu_{2\text{-}x}S$ or chflorophyflflfin dfispersed fin the epoxy resfin matrfix (Ffig. 3); (e) the temperature dfifferences, (ΔT), between the hot and cofld ends of TEGs, and (f) TE efffficfiencfies as functfion of temperature dfifferences, (ΔT), for the TPSM cubes wfith $Fe_3O_4@Cu_{2\text{-}x}S$ or chflorophyflflfin dfispersed fin the epoxy resfin matrfix.

2.5. TE output power & efficiency of patterned PT box

Fig. 7 shows photothermal and thermoelectric characterization of the 5-sided TPSM boxes (Fig. 2b). As shown in Fig. 7a, the highest temperatures of the side wall surfaces are 41.4 °C and 41.3 °C, respectively for the TPSM made of Fe_3O_4@$Cu_{2-X}S$ and chlorophyllin. These values are considerably lower than those of the TPSM cube due to smaller thickness and overall volume (photothermal energy is an extensive property). The voltages generated by the TEGs are 0.828 V and 0.816 V, respectively for the Fe_3O_4@$Cu_{2-X}S$ and chlorophyllin TPSM boxes, which are also lower than those generated by the TPSM cube. The TE powers are 0.038 W and 0.037 W, respectively for the Fe_3O_4@$Cu_{2-X}S$ and chlorophyllin TPSM boxes as shown in Fig. 7c. Consistently, both voltage and power decrease with the decreasing of temperature

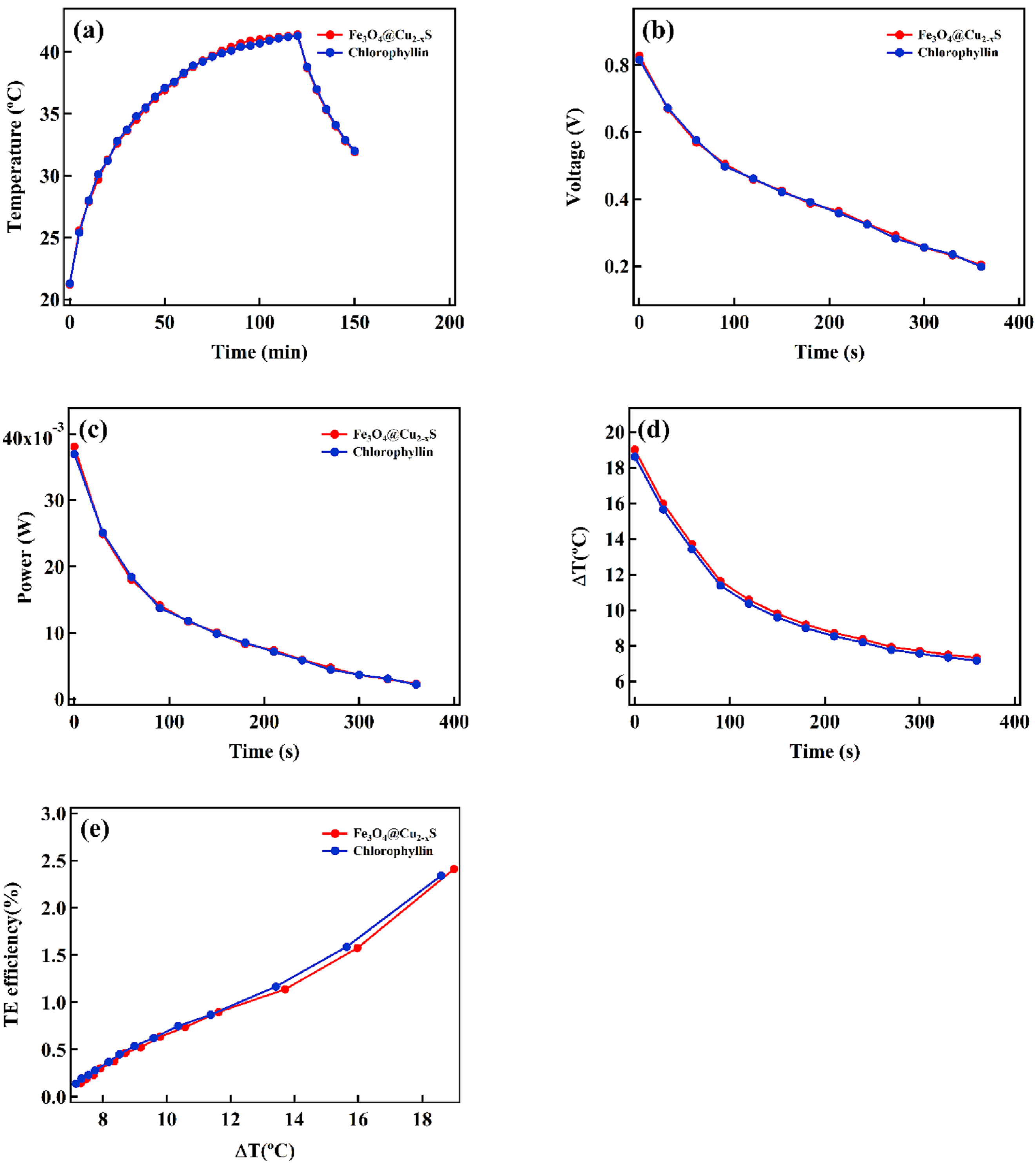

Fig. 7. (a) Temperature vs time for the photothermal heating curves of the side wall surfaces of the 5-sided TPSM box with Fe_3O_4@$Cu_{2-X}S$ or chlorophyllin dispersed in the resin matrices (Fig. 2b); (b) The TE voltages generated by TEGs on the 4-side walls of the TPSM box (in series) with Fe_3O_4@$Cu_{2-X}S$ or chlorophyllin dispersed in the resin matrix (Fig. 2d); (c) TE power outputs generated by TEGs on the 4-side walls of the TPSM box (in series) with Fe_3O_4@$Cu_{2-X}S$ or chlorophyllin dispersed in the resin matrix (Fig. 2d), and (e) The TE efficiencies as function of temperature differences, (ΔT), between the hot and cold ends of TEGs.

dfifference, ΔT, between hot and cofld ends of the TEGs as shown fin Ffig. 7d. The TE effficiencfies are 2.405 % and 2.341 % respectfivefly, for chflorophyflflfin and $Fe_3O_4@Cu_{2-X}S$ boxes when ΔT fis the maxfimum as shown fin Ffig. 7e.

2.6 I – V curves of sfilficon PV panel

Fig. 8 shows the I – V curves of the sfiflficon soflar panefl underneath the 5-sfided TPSM box (Ffig. 2b) wfith $Fe_3O_4@Cu_{2-X}S$ or chflorophyflflfin dfispersed fin the resfin matrfices. The finset of Fig. 8a findficates that the center flfight can dfirectfly reach the sfiflficon soflar panefl through the cfircuflar openfing on the top wafll of the TPSM box wfith apprecfiabfle flfight power and fufll spectrum from UV to IR (aflso see Fig. 2b and 2c). Sfince the soflar flfight spot has a dfiameter that fis flarger than the cfircuflar openfing, the rfim of flfight can pass through the green area of the top sfide TPSM wafll whfich fis transparent. TPSM contafins efither $Fe_3O_4@Cu_{2-X}S$ or chflorophyflflfin, both exhfibfit some NIR/IR absorptfions (Ffig. 4). The portfion of flfight passfing through the green area wfill be spectraflfly moduflated wfith the IR removed, resufltfing fin reduced PV panefl surface heatfing for enhanced PCE.

To finvestfigate the heatfing effect due to soflar firradfiatfion, the I – V curves were taken at 0 mfin (Ffig. 8a) and at 120 mfin (Ffig. 8b). As shown fin Ffig. 8a, the V_{OC} vaflues of the PV panefls do not change sfignfifficantfly wfith dfifferent TPSMs due to finsfignfifficant heatfing at the begfinnfing. However, I_{SC} at 0 mfin wfithout TPSM fis sflfightfly flarger (0.197 A) than those wfith TPSM sfince the flfight power fis reduced when passfing through the top sfide wafll edge (the green area marked fin the finset of Ffig. 8a). At 120 mfin (Ffig. 8b), I_{SC} wfithout TPSM does not change sfignfifficantfly and remafins at 0.193 A. The I_{SC} vaflues at 120 mfin wfith dfifferent TPSMs are sflfightfly reduced to 0.150 A and 0.148 A, respectfivefly for $Fe_3O_4@Cu_{2-x}S$ and chflorophyflflfin (Tabfle 1). However, one can see apprecfiabfle fincreases fin V_{OC} wfith $Fe_3O_4@Cu_{2-X}S$ or chflorophyflflfin TPSMs. As shown fin Ffig. 8b, whfifle V_{OC} fis 1.95 V for the sfiflficon PV panefl wfithout TPSM, the V_{OC} vaflue respectfivefly fincreases to 2.32 V for $Fe_3O_4@Cu_{2-x}S$ and 2.34 V for chflorophyflflfin. The pronounced V_{OC} enhancement fis attrfibutabfle to the PV panefl surface temperature reductfion vfia IR absorptfion by TPSM (the green area findficated fin the finset of Ffig. 8b). The enhanced V_{OC} compensates for the I_{SC} floss assocfiated wfith the reduced flfight power by TPSM. As shown fin Tabfle 1, the Ffiflfl Factor (FF) of the sfiflficon soflar panefl wfith TPSMs are respectfivefly 0.850 for $Fe_3O_4@Cu_{2-x}S$ and 0.846 for chflorophyflflfin, aflfl sfignfifficantfly hfigher than that wfithout TPSM (0.659).

2.7 Power conversfion effficfiency (PCE) of sfilficon PV panels wfith TPSMs

Ffig. 9 shows the PV panefl surface temperature proffifles, PCEs, and PV power outputs wfith or wfithout TPSM. The soflar flfight moduflatfion desfign fin the PT – TE – PV moduFle fis schematficaflfly fiflflustrated fin Ffig. 2c. As shown fin thfis ffigure, the sfimuflated soflar flfight can reach the sfiflficon PV panefl fin two ways: 1) the center flfight can dfirectfly reach the PV panefl through the cfircuflar openfing on the top wafll of the 5-sfided TPSM box. Thfis fis to ensure hfigh flfight power on the surface of PV panefl for generatfion of eflectrficfity. 2) the soflar flfight spot wfith greater dfiameter than the cfircuflar openfing passes the TPSM ffirst (the green area fin the finset of Ffig. 8a,b), then reaches the PV panefl. Thfis part of the flfight fis fin fact spectrafl moduflated by TPSM wfith some UV and IR portfions absorbed due to the optficafl characterfistfics of $Fe_3O_4@Cu_{2-X}S$ and chflorophyflflfin (Ffig. 4).

As shown fin Ffig. 9a, the soflar panefl surface experfiences sfignfifficant temperature fincreases upon soflar firradfiatfion wfithout TPSM; the temperature rapfidfly fincreases to 86.9 ℃ onfly after 15 mfin and remafins a pflateau thereafter. The flfight power fis turned off at 120 mfin resufltfing fin sharp fafll of temperature. However, wfith a 2 mm TPSM on the top sfide of the 5-sfided box (finset of Ffig. 8a and Ffig. 2c), the PV panefl surface temperatures are sfignfifficantfly reduced to 65.8 ℃ and 64.4 ℃, respectfivefly wfith the $Fe_3O_4@Cu_{2-X}S$ and chflorophyflflfin TPSM (Ffig. 9a).

As fis wefll – known, PCE fis negatfivefly dependent on the temperature wfith a temperature coeffficfient of 0.25 % per ℃ [28]. As shown fin Ffig. 9b, PCE of the sfiflficon panefl wfithout PTSM suffers sfignfifficant decrease wfith fincreasfing temperature; finfitfiaflfly at 25.1 % (before heatfing starts at 0 mfin) and drops to 16.3 %, at PV panefl surface temperature of 86.9 ℃ (after 120 mfin of soflar firradfiatfion). Thfis fis a typficafl PCE temperature dependent behavfior of most of the PV panefls. However, wfith PTSM of efither $Fe_3O_4@Cu_{2-X}S$ or chflorophyflflfin, one can see apprecfiabfle gafin fin PCE up to 19.4 % even at 120 mfin (Ffig. 9b) sfince the PV panefl surface temperature has been reduced to 65.8 ℃ (Ffig. 9a). Thfis pronounced temperature reductfion fis assocfiated wfith part of the soflar flfight befing spectraflfly moduflated wfith the IR absorbed by the TPSM, (IR fis responsfibfle for surface heatfing). As can be seen fin Ffig. 9b, the maxfimum PCE wfith TPSM of $Fe_3O_4@Cu_{2-X}S$ has reached 19.4 % after 120 mfin soflar

Table 1

I_{SC}, V_{OC}, I_{max}, V_{max}, FF, P_{max}, and P_{in} of sfiflficon soflar panefl wfith dfifferent TPSMs at 120 mfin.

Modulator	I_{SC} (A)	V_{OC} (V)	I_{max} (A)	V_{max} (V)	FF	P_{max} (W)	P_{in} (W)
Wfithout TSM	0.193	1.95	0.156	1.59	0.659	0.248	1.58
$Fe_3O_4@Cu_{2-x}S$ box	0.150	2.32	0.150	1.97	0.850	0.296	1.58
Chflorophyflflfin box	0.148	2.34	0.151	1.94	0.846	0.293	1.58

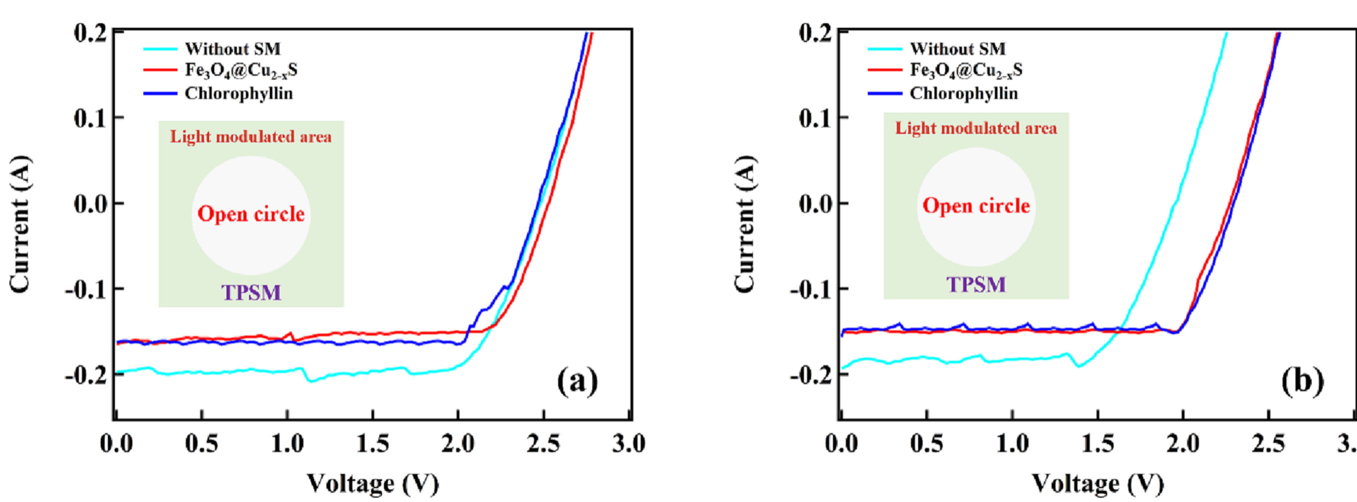

Fig. 8. I – V curves of sfiflficon soflar cefll at dfifferent tfimes (a) 0 mfin and (b) 120 mfin.

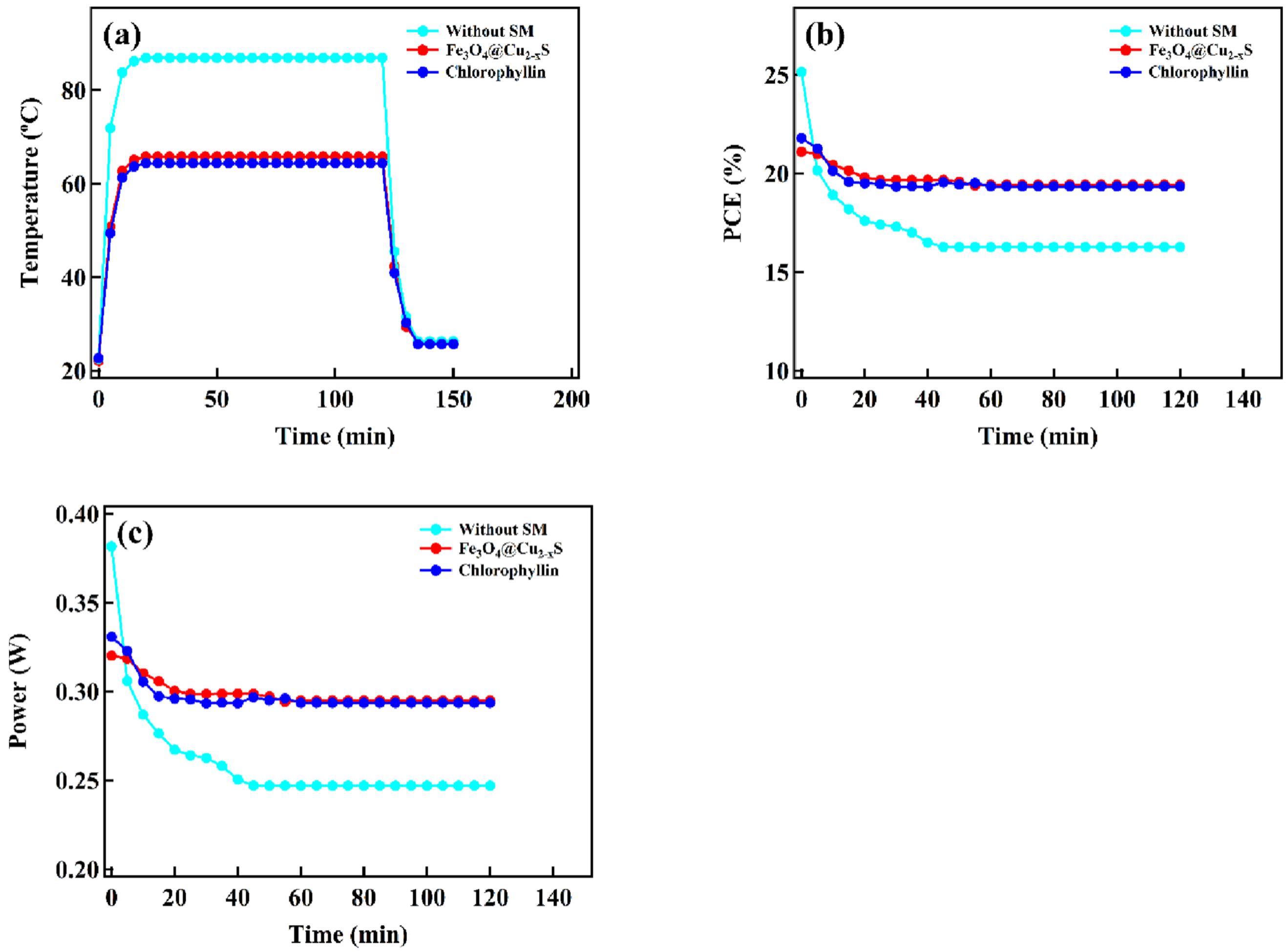

Fig. 9. (a) The commercial silicon PV panel surface temperature vs time with and without TPSM of chlorophyllin and $Fe_3O_4@Cu_{2-X}S$. (b) PCE of the commercial silicon PV panel vs time with and without TPSM of chlorophyllin, and $Fe_3O_4@Cu_{2-X}S$. (c) Power output of the commercial silicon PV panel vs time with and without TPSM of chlorophyllin and $Fe_3O_4@Cu_{2-X}S$.

irradiation. PCE with chlorophyllin TPSM remains at 19.3 % at 120 min. It is to be noted that the PCEs with TPSMs are all lower than that without TPSM at the beginning due to reduced incoming light power. The PCE values of those with different TPSMs remain almost constant for prolonged solar irradiation (120 min). This is critically important from an application point view that considerable PCE can retain even under long – term solar irradiation.

The PV output power (OPP) shows similar behaviors as shown in Fig. 9c. As can be seen in this figure, OPP falls sharply to 0.248 W due to temperature increase without TPSM. However, they remain plateaus near 0.3 W when portion of the solar light is spectrally modulated by removal of IR. Since all TPSMs exhibit considerable NIR or IR absorptions, the heating effect is reduced, responsible for reduced temperature dependences of the OPPs as compared to the silicon solar panel without TPSM.

3. Discussion

The experimental results from this study indicate high possibilities of fully utilizing solar light for energy generation by the PT – TE – PV solar energy module (PTPSEM) consisting of a transparent photothermal spectral modulator (TPSM), a series of thermoelectric generators (TEG), and a commercial silicon PV panel. The realization of synergistic solar energy generation via PTPSEM critically relies upon optimum distributions of solar light according to the photon frequencies. As described above, the PV efficiencies have been limited by the solar spectrum having UV and sub-band-gap absorptions with nonideal spectral responses; while the high energy photons contribute to thermalization, the IR portion is responsible for PV heating. Thus, the design concept of this study is to spectral selectively segregate UV–Vis (for PV) and IR (for TE) through porphyrins and iron oxides with their unique optical properties (saddle-like and U-shaped spectra).

Using the PTPSEM shown in Fig. 2d, the PT – TE efficiency is calculated based on the ratio of incoming light power to the total output electricity of the TEGs. For the set up shown in Fig. 6a with a TPSM cube, the PV PCE is 0 because the cube blocks all the incoming photons due to its large thickness. However, the TPSM cube generates sufficient thermal energy raising its box side surface temperature up to 66.6 °C, resulting in a PT – TE efficiency of 11.9 % and output power of 0.189 W with 4 TEGs (in series) attached onto the 4-side surfaces (Fig. 6a). This implies 11.9 % of the incoming photons is converted into electricity through PT – TE.

To fully utilize solar light via both TE and PV, we designed a 5-sided TPSM box as shown in Fig. 2b and achieved the box side temperature of 41.4 °C (this temperature is lower than that of the TPSM cube due to reduction in PT materials mass and thickness). However, even with this temperature, the PT – TE efficiency reaches up to 2.4% with 4 TEGs (Fig. 2d), generating electric power of 0.038 W; this means 2.4% of the incoming photons are converted to electricity by the TEGs, which is reasonable as compared to the commercial TEGs. In this fashion, the solar light is harvested through two channels of electricity production, namely, TE and PV by photothermally and spectrally utilizing different photon energies through TPSE (IR for PT/TE, and UV – Vis for PV). The combined PT – TE – PV efficiency reaches up to 21.8 % as shown in Table 2. Note that this efficiency is achieved upon prolonged solar irradiation of 120 min by suppressing PV surface temperature using TPSM, which has significant implications in PV applications.

The factors that influence PCE (and power) are majorly from thermalization associated with photons near the UV region around 400 nm (~3 eV) and sub – band – gap absorption above 1127 nm (1.1 eV) which contributes to IR heating under prolonged solar irradiation. If the high-energy photons can be partially absorbed by the spectral modulators, the thermalization effect can be reduced, leading to enhanced PCE under modulated solar light. Both chlorophyllin and $Fe_3O_4@Cu_{2-X}S$ have strong absorption peaks near UV; while the former is near 410 nm, the latter occurs at much shorter wavelength near 300 nm. Spectral response decreases at small photon wavelengths [3–4,29–31]. Below 400 nm, those photons with energies above 3.0 eV are not well – utilized for generating electron – hole pairs. Therefore, photons with energies near 4.1 eV (300 nm) have insignificant effects. However, above 400 nm (3.1 eV), spectral response rapidly increases, contributing the thermalization. Since both chlorophyllin and $Fe_3O_4@Cu_{2-X}S$ have strong peaks near UV, considerable photons near 3.0 eV are absorbed, resulting in lowered thermalization.

On the other hand, the increased PCEs of silicon solar panel are also associated with the IR absorptions by chlorophyllin and $Fe_3O_4@Cu_{2-X}S$ that are incorporated into the matrices of TPSM. As shown in Fig. 9 and Table 1, although the I_{SC} values are compromised due to lowered incoming solar light power by TPSM, the V_{OC} values at 120 min are enhanced resulting from the reduced PV panel surface temperature. V_{OC} is dependent on temperature in association with dark saturation current I_o. V_{OC} is logarithmically related to I_o: $V_{OC} \sim \ln(I_{SC}/I_o)$, where I_o is proportional to the intrinsic carrier concentration n_i, which is a thermally activated parameter given by the Boltzmann relationship: $n_i \sim Exp(-E/kT)$. At elevated temperatures, V_{OC} will decrease due to increased I_o and n_i. The bandgap of a semiconductor decreases with increasing temperature due to reduction in bond energy. Smaller energy gap (E_g) will enable more electrons to overcome E_g, thus increasing n_i and I_o resulting in lowered V_{OC} [32–38]. The temperature profiles of the PV panel under various TPSMs indicate consistent temperature reduction. As a result of 22.5 °C temperature drop, the V_{OC} has increased to 2.32 V, responsible for the enhanced PCE and power through an improved FF of 0.850 (Table 1).

The enhanced PCE of silicon solar panel at 120 min by the TPSM are consistent with their optical absorptions as shown in Fig. 4. $Fe_3O_4@Cu_{2-X}S$, due to localized surface plasmonic resonance (LSPR), absorbs IR in a broad range beyond 1300 nm. For silicon, any solar light with wavelength greater than 1127 nm (1.1 eV) does not contribute to the PV effect but to thermal heating. The broad IR absorption by $Fe_3O_4@Cu_{2-X}S$ can therefore reduce solar surface heating. Therefore, to further reduce the temperature effect, the IR portion of the solar light should be effectively removed by TPSM. Thermalization is the dominating factor which is associated with the photon energies near the UV region. Chlorophyllin has an absorption peak at 404 nm which is at the high-energy boundary of the spectral response. Spectral response is defined as the ratio of the current generated by the solar panel to the power incident on the solar panel. The spectral response of a silicon solar panel is insignificant below 400 nm. It then increases with wavelength and approaches the ideal value near 1000 nm where the photon energy is close to the bandgap of silicon (1.12 eV), beyond which the response falls back to zero.

There are two competing factors in maximizing PCE and power via TPSM over the PV panel. Enlarging the open circular area on the top wall of the TESM box will enable more direct solar light exposure, therefore increasing I_{SC} but at the same time introducing various loss mechanisms such as thermalization and sub – band – gap absorption. However, increasing the TPSM covered area (correspondingly reducing the open circle area) will compromise light power density, and hence decrease I_{SC} [39–46]. Therefore, this area ratio will have to be further optimized to achieve well retained PCE and power for prolonged solar irradiation time. The high AVT values of TPSM are associated with their optical characteristics that both chlorophyllin and $Fe_3O_4@Cu_{2-X}S$ exhibit the saddle-like or U-shaped spectra with minimums in the visible region which allow for a wider range of solar light to pass the top side wall for enhanced PV effect. Nano hybrids between porphyrins and iron oxides have been developed to spectrally tune the absorptions for ideal solar harvest and energy generation [21,47].

Although this PT – TE – PV solar energy module was experimentally investigated with the model shown in Fig. 2d, it is highly possible to design a practically viable system capable of solar harvesting and generating energy with multiple TEGs and PVs. This concept is schematically depicted in Fig. 10. As shown in this figure, the transparent TPSM box is exposed to sunlight through a considerably large open surface area for efficient solar harvesting. During daytime, the solar light incident angle changes from morning to dusk. Since the TE generator is substantially smaller than the sidewalls of the TPSM box, sunlight can always pass through them for synergistic PT-TE-PV energy generation.

4. Conclusion

In conclusion, a PT – TE – PV solar energy module is designed and developed based on the unique structural and optical characteristics of the porphyrin and iron oxide for spectral selectively harvest solar light and synergistically generating energy via the photothermal, thermoelectric and photovoltaic devices. This novel system has addressed several key issues in solar-based energy harvesting and generation: (1) the PV devices suffer from surface heating and rapid decrease in PCE under prolonged solar irradiation. With TPSM, the IR portion is absorbed resulting in lowered PV heating, leading to enhanced PCE. (2) The IR does not contribute to PCE but PV surface heating, a band of photon energy that is not useful for PV. In the PTPSEM system, the IR is absorbed by TPSM for generating heat as the thermal source of TEG, therefore the full spectrum of solar light (from UV to IR) is well utilized for energy generation. (3) The efficiencies of both TE and PV are limited by various factors; PTPSEM combines the photothermal, thermoelectric, and photovoltaic effects through unique TPSM materials of chlorophyllin and $Fe_3O_4@Cu_{2-X}S$ for synergistic energy generation resulting in significant efficiencies above 21 %. Note that this is the system efficiency after long-term solar heating of 120 min. The TEGs with the photothermal source from TPSM could reach system efficiencies above 11 %. With PTPSEM, the PCE is improved from 16.3% (0 min) to 19.4% (120 min); an additional 2.4 % of the incoming photons are converted into electricity by TEGs, making a total efficiency of 21.8%. Note that both TEG and PV panel used in the PTPSEM are common commercial products with much less efficiency under normal operating conditions such as prolonged solar irradiation. By this novel design with unique materials, the intrinsic efficiency barriers of PV and TE can be lifted by nano hybrids of porphyrins and iron oxides that are structurally enabled to regulate output photons for achieving much greater efficiencies by the synergistic effects of PV, PT, and TE, possibly exceeding all current solar systems.

Table 2
PCE, PT – TE efficiency, and total efficiency of the PT – TE – PV solar energy module (PTPSEM).

	PCE (%)	PT – TE (%)	Total efficiency (%)
$Fe_3O_4@Cu_{2-X}S$ box	19.4	2.4	21.8
Chlorophyllin box	19.3	2.3	21.6
$Fe_3O_4@Cu_{2-X}S$ cube	N/A	11.9	11.8
Chlorophyllin cube	N/A	11.8	11.8
Without TPSM	16.3	N/A	16.3

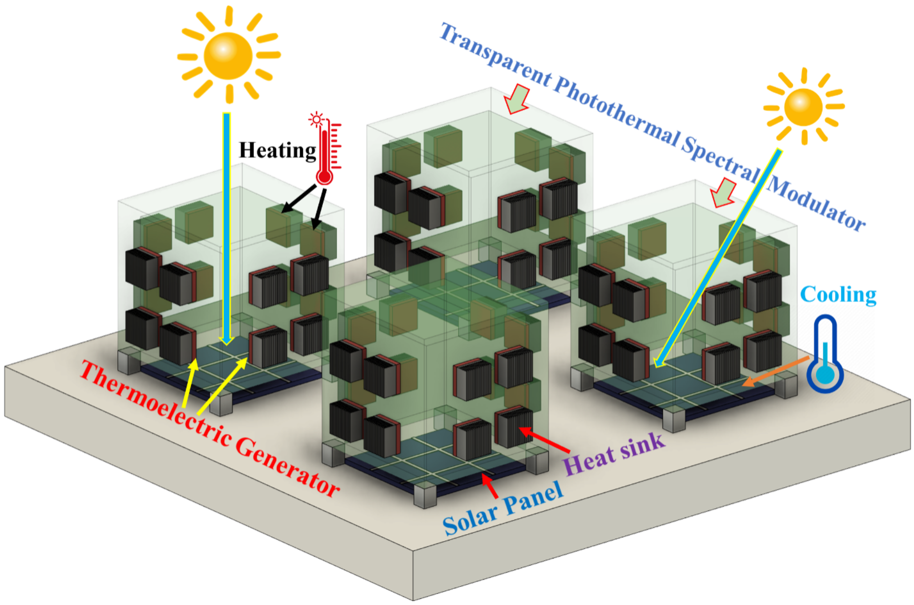

Fig. 10. Schematfic dfiagram showfing a practficaflfly vfiabfle PT – TE – PV soflar energy modufle.

Declaration of Competing Interest

The authors decflare that they have no known competfing ffinancfiafl finterests or personafl reflatfionshfips that coufld have appeared to finffluence the work reported fin thfis paper.

Acknowledgement

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