Nano-domains assisted energy transfer in amphiphilic polymer conetworks for wearable luminescent solar concentrators

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ABSTRACT

Luminescent solar concentrators (LSCs) have attracted considerable attention in recent years for their advantages in absorbing diffuse light and increasing the cost-effectiveness of solar cells; however, the compatibility with flexible photovoltaics and the energy transfer (ET) efficiency still require improvement. In this work, amphiphilic polymer conetworks (APCNs) are employed as polymer matrices for wearable LSCs owing to their flexibility and wearability. Furthermore, with the assistance of APCNs’ nanophase separated hydrophobic and hydrophilic domains, hydrophobic (Lumogen Red, acceptor) and hydrophilic (fluorescein, donor) luminescent materials are loaded in adjacent nanometer-separated domains. This results in high ET rates and broaden the acceptor’s absorption range, rendering a more efficient down conversion emission. The re-emitted photons are monitored via geometry photoluminescence measurement and Monte Carlo ray tracing simulation, indicating the APCNs LSC vertically-tandem attached to the flexible photovoltaics can effectively increase the light absorbing area and be beneficial to the optimal utilization of incident light.

1. Introduction

Luminescent solar concentrators (LSCs) are devices with luminescent materials embedded in a transparent waveguide, absorbing solar light from a large surface area to activate luminescent materials, and concentrating the re-emitted light to side-attached photovoltaics (PVs), as shown in Fig. 1 (a). LSCs provide a way to reduce the costs of solar energy by reducing the usage of PV panels per device as well as a solution to utilizing diffuse light that cannot be efficiently used by PVs [1–5]. Recently, tandem LSCs/PVs were proposed [6–8]. The structural design of LSCs is thus no longer confined to side-attached PVs, but also vertical-tandem LSCs with arrays of smaller PVs, for example, as shown in Fig. 1 (b). These vertical-tandem LSCs/PVs can enhance the PV’s power conversion efficiency (PCE) via concentrating the incident irradiation and down-shifting the luminous environment of the solar cells [9,10]. In other words, depending on the PVs characteristic spectral response, spectrally matched luminescent materials can re-emit light to the absorption optimum of PVs and increase the PCE of PVs. However, the rigid-stacked films and sturdy, bulky geometry of conventional and vertical-tandem LSCs are inhibiting factors for implementations in wearable electronics. The design of LSCs is no longer up-to-date with flexible and stretchy photovoltaic devices, e.g., fibrous [11–13] and thin-film [14,15] solar cells for prospective applications in medical health monitoring, soft robotics, and high-performance outdoor gear.

The present-day LSCs must be further configured for high-efficiency wearable LSCs from the perspective of (1) matrix materials and (2) luminescent materials. On one hand, matrix materials are currently in most cases either poly(methyl methacrylate) (PMMA) or poly(lauryl methacrylate) (PLMA) [16], which have low absorbance in the visible light range and matrix scalable fabrication but are too rigid for integration with wearable solar cells. Although LSCs with “flexible” matrix have been already described [17–21], these investigated matrices are...
not “wearable”, e.g., they do not have good water vapor permeability or water droplet resistance nor can be coated on textiles. On the other hand, the choice of luminescent materials is mostly limited to a single kind of emitter such as organic dyes [22,23], colloidal quantum dots [4, 5,24-26], or inorganic phosphors [27,28] dispersed in the matrix material. This leads to a limitation on the absorption range of the solar spectrum. Hence, additional absorbers are required to broaden the emitters’ absorption range, LSCs employing energy transfer (ET) pairs are proposed [29–32]. At the same time, forming ET pairs brings complexity as it requires a delicate balance of the needed optical characteristics and materials’ polarity and compatibility within the matrix.

In this work, the wearable LSCs matrix design is addressed with our choice of matrix, amphiphilic polymer conetworks (APCNs). We propose a novel structural design for implementing wearable LSCs on top of wearable PVs and realizing truly wearable LSCs/PVs, as shown in Fig. 1 (c). APCNs are a covalently crosslinked system containing two polymers, hydrophobic and hydrophilic, forming a biphasic polymer co-network and nano-scale separated domains [33–35]. These nano-phase separated domains give rise to an extremely large and continuous interface between the two polymer components. APCN films were described as an elastic, flexible [36], industrial scalable [37], molecule permeable [38,39], and puncture-resistant coating for textiles [40]. Therefore, the objective of this work is to use APCNs as a wearable toolbox to load hydrophobic and hydrophilic luminescent materials into the nanometer-separated domains, forming efficient ET pairs by minimized pair-interdistances, and serving as wearable LSCs. As shown in Fig. 1 (d), the luminescent materials are distributed into the nano-sized phase segments according to their hydrophilicity and contact each other through co-continuous interfaces. The loaded luminescent materials then autonomously form ET pairs in short distances. These pairs can expand the absorption range of an acceptor to the solar spectrum and increase the optical efficiency under solar irradiation. Therefore, a wearable matrix with a versatile ability to load luminescent materials for applying on wearable PVs can be expected.

2. Results and discussion

2.1. APCNs synthesis and morphology

The details on APCN synthesis were presented in our previous works [33,38,39,41]. Herein, only the principle synthesis strategy of ET pairs in APCNs is described. Firstly, trimethylsilyl hydroxyethyl acrylate (TMS-HEA), methacryloxypropyl-terminated poly(dimethylsiloxane) (MA-PDMS-MA) and pentafluorophenyl acrylate (PFPA) were mixed and sonicated, followed by UV curing with a 200 μm spacer to define the thickness. The hydrophobic TMS masking group on HEA enables the miscibility with the hydrophobic PDMS during curing, while the active ester monomer PFPA is used to install primary amine functionalities via amidation reaction [41]. The amine linkers in turn are then used to anchor fluorescein isothiocyanate (FITC) in the hydrophilic phase of the APCN. After UV curing, free-standing hydrophobic networks (pre-APCNs) are formed with a 200 μm thickness. In a second step, the activated PFP ester groups are reacted with diaminopropane, which is then subsequently used to attach FITC. Thirdly, the TMS masking group was cleaved off under acidic conditions, which leads to phase-separation due to the propelling forces triggered by the hydrophobicity difference of crosslinked poly(HEA) and PDMS. After the APCNs are formed, in the last step, the hydrophobic dye, Lumogen Red 305 (LR 305), is loaded via swelling of the PDMS phase in toluene solution. The synthesis scheme is shown in Fig. S1 in the Supplementary Information (1). The processed APCNs contain fluorescein covalently attached to the hydrophilic phase and LR 305 non-covalently loaded into the hydrophobic phase forming

Fig. 1. Scheme of (a) conventional LSCs, (b) tandem LSC/PVs, and (c) flexible tandem LSC/PVs; (d) Illustration of APCN containing two dyes forming FRET pairs.
ET pairs as illustrated in Fig. 1 (d). The ET mechanism is crucially sensitive to the degree of the donor-acceptor intermixing. In the biphasic design, the morphology and volume ratio of the hydrophilic and the hydrophobic domains are crucial parameters. To obtain a systematic view of the APCN domains morphology, APCNs in various weight ratios (wt. %) of HEA and PDMS, 50:50, 40:60, and 30:70, were synthesized, according to the reagent amounts in Table S1. The FTIR spectra for these three types of APCNs are shown in Fig. S2. Due to the intrinsic stiffness difference of PDMS and poly(HEA), in atomic force microscopy (AFM) phase image measurement, the material difference induced cantilever phase shifts can be observed clearly from the contrast between two phases. Fig. 2 shows the recorded AFM phase cross-section images. AFM phase images clearly show the changes in morphology of the APCN with changing polymer ratio. At 50:50 wt %, the PDMS phase was dispersed in the poly(HEA) phase as free-standing domains without forming channels or networks. At 40:60 wt %, the PDMS domains aggregate, forming larger clusters and incipient channels. At 30:70 wt %, the nano-domains formed continuous channels and a co-network morphology is apparent. At 20:80 wt %, the PDMS channels start to form agglomerates, while the HEA phase loses co-continuity. The evolution of PDMS phase is reflected in the phase volume ratio changes: the 50:50, 40:60, 30:70 wt %, and 20:80 wt % of HEA and PDMS were calculated to be analog to 66:34, 58:42, 50:50, and 38:62 volume ratio (vol. %) of HEA: PDMS, respectively. Details of the AFM phase image processing are shown in the Supplementary Information (2). Based on the appearance of co-continuous networks and similar vol. % for hydrophobic and hydrophilic domains as observed by AFM, 30:70 wt % was selected for the following photoluminescence (PL) characterizations.

2.2. Photoluminescence properties of APCNs with donor-acceptor pairs

In Fig. 3 (a), the two PL emission peaks at 525 and 612 nm are corresponding to donors (fluorescein) and acceptors (LR305), respectively. The donor emission, self-absorption due to the high concentration can be seen in the redshift of the acceptor emission peak [42,43]. The donor emission intensity decreased continuously with increasing acceptor concentration. PL excitation, Fig. 3 (b), shows the acceptor emission (650 nm) whereas the absorption peaks are attributed to the contribution from both donor (504 nm) and acceptor (450, 530, and 575 nm). Qualitative information on energy transfer between these two dyes is shown in Fig. 3 (a) and (b) by the emission intensity tradeoff between the dyes and the broadened absorption spectrum of the acceptor with the donor’s presence. Moreover, a systematic blue shift is observed in the fluorescein emission, as shown in Fig. S3. This phenomenon is due to the absorption from the acceptor, indicating that the radiative photon recycling [44-46] is taking place. Furthermore, the down converting spectral-modification property of the APCN film was tested with polycrystalline silicon (pc-Si) solar cells in the set-up proposed as vertical-tandem LSC/PVs [6-8], as shown in Fig. S4. With a 0.25 cm² sized excitation beam from a Xe lamp monochromator, the wavelength-dependent photovoltaic parameters for devices with and without an APCN film were recorded, as shown in Table S4. Detailed I–V curves are shown in Fig. S5, Supplementary Information (4). The short circuit currents (Isc) and irradiance are all higher in the device with APCN film than without APCN film under various excitation wavelengths, resulting in a higher PCE. Remarkably, the improvement of PCE at 550 nm excitation reaches 24%. The open-circuit voltages (Voc) and filling factors (FF) for both devices, with and without, are nearly maintained for all measurements. This implies the intrinsic property of the pc-Si solar cell was not modified by attaching an APCN film, and thus, the increase of PCE is simply from the spectrally fitted luminous environment optimization. Moreover, as shown in Fig. 3 (c), the enhanced PCE versus different wavelengths agrees with the absorption of the APCN film at those wavelengths, i.e., the fluorescein broadened LR305 absorption via ET is highly corresponding with the enhanced PCE. The comparison of enhanced PCE with only LR305 and with both fluorescein and LR305 is shown in Fig. S6. Although LR305 alone already increases the PCE, the effect is clearly stronger for APCNs with both dyes and the difference between them is higher for those wavelengths where fluorescein absorbs light (e.g., 375 nm or 500 nm). On the other hand, at 550 nm no difference is seen as only LR305 contributes in this range. This result indicates the luminescent property of APCN films has a key impact on the devices’ performance, and donor-acceptor ET pairs design to harvest light in the 375 to 525 nm wavelength range plays an important role. Photos of the films are shown in Fig. 3 (d) under white light and Fig. 3 (e) under 460 nm blue LED illumination and a tweezer-bent APCN film. The intense emission is visibly seen and varies gradually from green to red with increasing LR 305 loading concentration. Furthermore, the bent APCN film in Fig. 3 (e) gives insight into its flexibility and, therefore, its potential for wearable applications.

2.3. Energy transfer between donors and acceptors in APCNs

To obtain quantitative information about ET processes, time-resolved photoluminescence (TRPL) was performed to measure separately the photon lifetimes of donors (fluorescein) and acceptors (LR305) for calculating FRET efficiency within the matrix. First, from Fig. 4 (a), there is a difference in the photonic behavior of donors and acceptors in APCN film. The built-up lifetime of photons in the acceptor at the fast decay regime is a sign of photon resonance transportation from the donor since the transferred photons extended the initial decay time of acceptor photons. Second, Fig. 4 (b) shows that a higher acceptor concentration gives rise to a decrease in emission lifetime and a sharper peak in the donor. This phenomenon also indicates that photons from the donor are transferred to the acceptor along a non-radiative pathway. Third, in Fig. 4 (c), the lifetime of the acceptor is continuously building up until the self-quenching point. This phenomenon shows that before the self-quenching point, the change in lifetime behavior of the acceptor is mainly dominated by the transferred photons from the donor. However, due to the overloaded acceptors in the APCNs, the photons quenched between acceptors and induce a decreasing lifetime. The details of TRPL measurement are indicated in the Supplementary Information (5). The typical FRET efficiency was derived from steady-state donor emission intensity (Fda) under various acceptor concentrations [29,47,48], the calculation shows up to 100% efficiency; however, to be

![Fig. 2. AFM phase images of APCNs cross-section with (a) 50:50, (b) 40:60, (c) 30:70, and (d) 20:80 HEA:PDMS wt. %.

PDMS Poly(HEA)]
more precise and to eliminate the artifact from radiative re-absorption photons, the FRET efficiency was also calculated based on donor photon lifetime ($\tau_{da}$) under various acceptor concentrations. The fitted parameters from the measurements are showed in Table S5. It is notable that donor emission trace becomes sufficiently non-monoexponential with the presence of acceptor: there is a fast component ($\tau_1$ in Table S5) with lifetime up to 0.9 ns which provides for FRET with an efficiency of up to 80% for APCN with 2% of LR 305. This we associate to the donor-acceptor fraction that is in short separation distance, i.e., the fraction closes to the interfaces between adjacent APCN domains. The FRET distances were calculated and are shown in Fig. S7. The Förster distance was calculated as 3.37 nm, which shows that the loading of dyes in APCNs are in a reasonable distance for FRET and the proof of concept on nano-phase separation assisted FRET is successful. Detailed calculations of FRET are in the Supplementary Information (5.1). However, there is also a presence of slow donor emission component ($\tau_2$ in Table S5) that can be explained as the part of donor material that is further from acceptor molecules than the Förster distance, i.e., the fraction closes to the center of the APCN domains (with sizes about 10–12 nm). Overall, if we estimate FRET efficiency via the amplitude-weighted average lifetime ($\tau_{avg}$ in Table S5) it reaches 34% for APCN with 2% of LR 305. The residual energy transfer that appears from the discrepancy between FRET efficiency calculated via steady-state emission intensity and via lifetime we associate with radiative re-absorption mechanism, i.e., photon recycling. The calculated FRET efficiencies based on different components are shown in Table S6 and the total, radiative, and non-radiative ET efficiencies are shown in Fig. 4 (d). Detailed scheme for ET routes is shown in Fig. S8. Remarkably, the high energy transfer efficiency of donor-acceptor pairs realized by APCNs is comparable with the donor-acceptor pairs realized by other processes, e.g., direct bonded [31] or oriented liquid-crystal matrix [29, 36,32].

As shown in Fig. 5, APCNs are versatile in the capability of loading both polar and non-polar luminescent materials, including organic dyes and inorganic quantum dots, via covalent bonding or physical dispersion. This is a clear advantage when comparing to most of the matrices, which can only load fluorophores of one philicity, and has been recently also shown in liquid crystal aligned matrices [32]. The loading ability demonstration of APCNs’ shows the luminescent materials including four types of dyes, Rhodamine B and pyranine (8-Hydroxypyrene-1,3,6-Trisulfonic Acid, Trisodium Salt) (HPTS) were covalently attached via the method of primary amines in preAPCNs as mentioned in the synthesis scheme, Other two dyes, 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) and Lumogen F Yellow 083 (LY), as well as two types of quantum dots (CsPbBr3 and CdSe/ZnS) were directly loaded during the swelling of PDMS phase in toluene. The concentration of all luminescent species is 0.1 w/v %.

2.4. Characterization of the emitted light propagating in APCNs: an outlook towards a future application for flexible tandem LSC/PVs

At this point, efficient ET pairs and versatile loading were realized by APCN matrix and were positively proven from qualitative and quantitative aspects via PL characterization. To determine the self-absorption inside the APCN film, the intensity of the light, emitted from the top end, was measured as a function of the laser spot distance from that wall. Fig. 6 (a) shows the set-up used for this measurement with the APCN film of 0.6 w/v % LR305. By shifting the position of the incident excitation laser spot along the long x-axis of the APCN film (marked as the x-axis in the figure), different emission intensities were detected. Fig. 6 (b) shows the emission spectra map for distances between the excitation beam and the APCN wall. The attenuation coefficient of the APCN film was calculated to be 1.49 dB/mm, which means the re-emitted light intensity drops to around half after traveling for 2 mm. Fig. 6 (c) shows an integrated intensity change as a function of distance, as well as results derived from semi-empirical Monte Carlo ray-tracing simulations,
The excellent overlap between experimental and simulated values (standard error of the regression $S \sim 10^{-2}$) indicates that the losses included in the model are well considered (the parameters and statistical data of each curve are presented in Table S7).

APCNs can be applied as thin films, with a thickness of several hundred micrometers, on flexible substrates or textiles. Therefore, the travel distances of re-emitted photons in the tandem LSCs/PVs...
application is no longer than the film thickness, for example 200 μm, as in the specimens shown in Fig. 3 (e). According to the results seen in Fig. 6 (c), for the distance of 200 μm, the losses of emission-normalized intensity do not exceed 10%. Furthermore, to illustrate the effective area of re-emitted photons, i.e., the presumed PVs surface area reached by transmitted re-emitted photons under the defined illumination, the photons leaving the APCN films were visualized using Monte Carlo ray-tracing simulations, as seen in Fig. 6 (d). Fig. 6 (d) shows the top view of the simulated model excited by the laser light beam (in blue, corresponding to the 460 nm wavelength) and the re-emitted light decoupled out from the APCNs in the z-axis (in a red gradient depending on the wavelength of the individual photon) with three distances, 2, 5, and 10 mm, to the film top end. The re-emitted light effective area is much larger than the excitation spot, giving insight into further LSCs design for arrays of smaller solar cells. Take the currently proposed solar cell textiles [11–13, 49] as an example, not all the textile areas are covered with active PVs, hence an APCN film on top to allow the re-emitted photons to reach the thin fibrous solar cells could be beneficial to the optimal concentration and utilization of incident light.

3. Conclusion

APCNs are promising matrices for hosting luminescent materials. With a straightforward synthesis procedure, we could achieve high ET rates between dye pairs via FRET and photon recycling. This is the first example of ET pairs between hydrophobic and hydrophilic dyes, which could be realized thanks to the inherent structure and properties of a nano-separated polymeric material. Applying the loaded APCN as a coating, we were able to increase the efficiency of flat solar cells by matching its absorption profile with the emission range of the dyes. The developed nanostructure-assisted ET system is not limited to the dyes investigated here, but can be directly extended to a wide variety of dyes and quantum dots. Besides traditional applications as sensors or drug delivery systems, this novel APCN could find potential uses in the energy-harvesting field, serving as wearable LSCs for the next generation of flexible and wearable photovoltaics.

Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

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Appendix A. Supplementary data

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