Preparation and characterization of down-shifting film for silicon solar cell based on the stilben 420, PVA polymer and silver nanoparticles

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We have developed method of preparation of luminescent polymer films based on polyvinyl alcohol (PVA), organic dyestilben 420 (St420) and silver nanoparticles (AgNPs). Concentration of St420 which provides most efficient luminescence quantum yield was determined for PVA film. It was found that addition of 10 nm AgNPs to St420 samples in PVA leads to increase of absorption intensity and decrease of luminescence intensity. Quenching of emission of St420 by addition of AgNPs is probably due to charge transfer from the dye to metal nanoparticles. External quantum efficiency (EQE) curves of St420 PVA were measured for optimal concentration of the dye. Some decrease of EQE curve was observed for down-shifting (DS) layer of St420. At the same time some increase of efficacy ofsolar cell (SC) was observed based on I-V measurements.

Keywords: Down-shifting layer, silver nanoparticles, organic dye, solar cell.

Introduction

Maximal effectiveness of silicon solar panels is theoretically limited by 31% due to spectral losses [1], which arise from the limited spectral response (SR) of solar cells to the wideband solar spectrum. The best experimental one-sun devices fabricated in laboratories have achieved conversion efficiencies of 24.7% for wafer-based crystalline silicon (c-Si) cells [2]. However, there is opportunity to increase this value by making better use of short-wavelength light.

There are two principal approaches to achieve a more efficient utilization of the solar spectrum. The first is to improve the electronic properties of existing devices, using advanced design concepts [3-6]. The second approach is luminescent downshifting (LDS) of the incident spectrum: absorbing short wavelengths photons and re-emitting them at more favorable wavelength before they reach the cells.

Basically LDS consist of transparent matrix serving as a host material for luminescent substances.

For these purposes the chosen materials were indeed many, with the most frequent categories being polymers such as polymethyl methacrylate (PMMA) [7–9] or poly-vinyl acetate [10,11], and they can exhibit high transparency in the visible

region of the spectrum, adequate resistance to heat and humidity variations, and high mechanical strength [12]. They also provide very good host environment for organic dye molecules [13].

A large number of luminescent materials have been investigated for LDS and can be separated into three main categories: quantum dots (QDs) [14–18], organic dyes [7–9] and rare-earth ions/complexes [19–21].

QDs exhibit a wide absorption band, high emission intensity, relatively good photostability [18]. On the other hand, they result in high re-absorption losses due to their large overlap of absorption and emission bands, exhibit relatively poor luminescent quantum yield (LQY) and they remain generally expensive [22].

Organic dyes exhibit relatively high absorption coefficients [23] close to unity LQY [24]. And are easy to process in polymeric matrices [23, 24]. Their drawbacks are their narrow absorption bands and their relatively small Stokes-shift, which still results in significant re-absorption losses [25]. Rare-earth ions exhibit high LQY [22, 26], but have extremely low absorption coefficients [26].

Introduction of dye St-420 in PVA.

The dye stilbene 420 (St-420) has the structure which is presented in Figure 1.
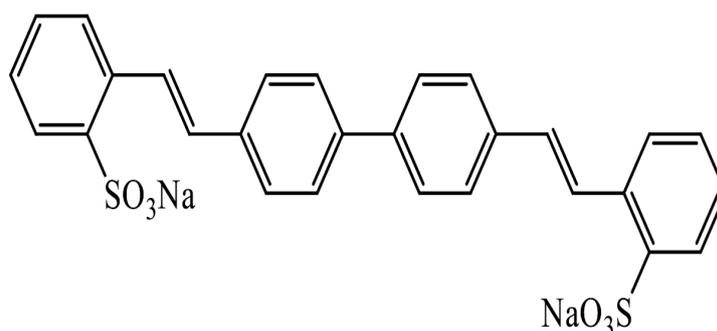

Figure 1. Structure of the dye stilbene 420 (St-420).

We have used water (Aq) as a solvent for PVA beads and for St420 methanol was used. Basic parameters of solutions are shown in Table 1.

Table 1.
Basic parameters of solutions of St420 in PVA.

#	1	2	3	4
m(solution), g	0.5883	0.5905	0.5888	0.6028
W(PVA in solution), %	3.37	3.32	3.37	3.28
W(St420 in PVA), %	0.15	0.30	0.59	1.19

Using these solutions we have obtained samples of films of St420 in PVA on a glass slide. Spectra of absorption and fluorescence of samples are shown in Figure 2, which shows that gradual increase of the dye concentration in polymer matrix in the considered range of concentrations leads to increase of absorption intensity. The shape of spectra remains constant. Similarly during the increase of concentration the emission intensity increases (Figure 2). Therefore one may suggest that in this range of concentration the aggregation of the dye molecules

does not take place. The maximum of the dye emission is at 440 nm and absorption peak is at (375-380) nm. Taking into account these spectral properties of the dye one may suppose that thin polymer film containing this dye could be used for photovoltaic cells which have highest sensitivity in a range (450-750) nm.
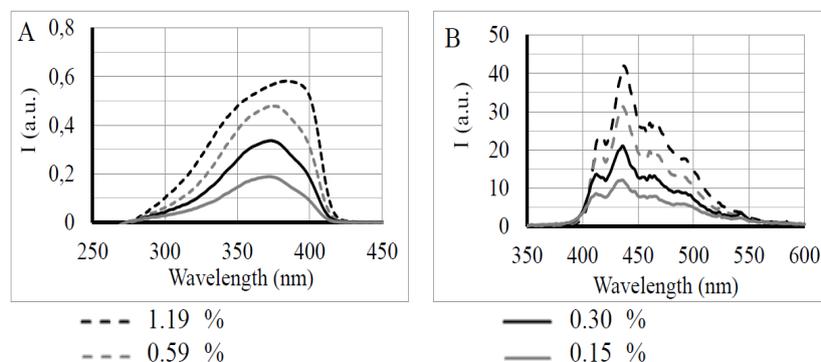

Figure 2. Spectra of absorption (A) and fluorescence (B) of PVA samples containing St420.

Introduction of dye St-420 and silver nanoparticles in PVA.

It is known that due to surface plasmon resonance (SPR) addition of metal nanoparticles (gold or silver) to polymer compositions of organic dyes may lead to enhancement of emission intensity. Therefore in accordance with the described method we have prepared samples containing St420 and silver nanoparticles (AgNPs) of size 10 nm using PVA. Basic data on concentrations and components ratios in experimental samples are shown in Table 2.

Table 2.
Basic parameters of solutions containing PVA, St420 and AgNPs.

#	1	2	3	4
m(solution), g	0.5865	0.6020	0.5891	0.5722
W(PVA in Aq), %	3.21	3.32	3.27	3.17
W(St420 in PVA), %	0.31	0.31	0.31	0.31
W(AgNPs to St420), %	0.00	1.57	3.30	7.12

Using these solutions the thin films were obtained. For these samples we have measured spectra of absorption and fluorescence (Figure 3).

As one can see from Figure 3A gradual increase of concentration of AgNPs provides increase of absorption in a range of (330–500) nm. And the peak of absorption is at 370 nm as in case of samples of St420 in PVA without metal nanoparticles (NP). Emission intensity decreases as the AgNPs concentration rises according to data from Figure 3B. Thus, we may assume that addition of AgNPs of 10 nm size to DS based on PVA composition of St420 in this range of concentrations does not improve the efficiency of PET since the presence of metal NP in this case provides quenching of dye St420 emission.

DS on the basis of St-420.

Next we have tested effect of DS containing dye St420 demonstrating more longwavelength emission than dye BBQ. We have prepared 4 samples of DS, containing different concentrations of St420. EQE for sample with maximum concentration of the dye is shown in Figure 4.

Ratio of mass of AgNPs to mass of St420:

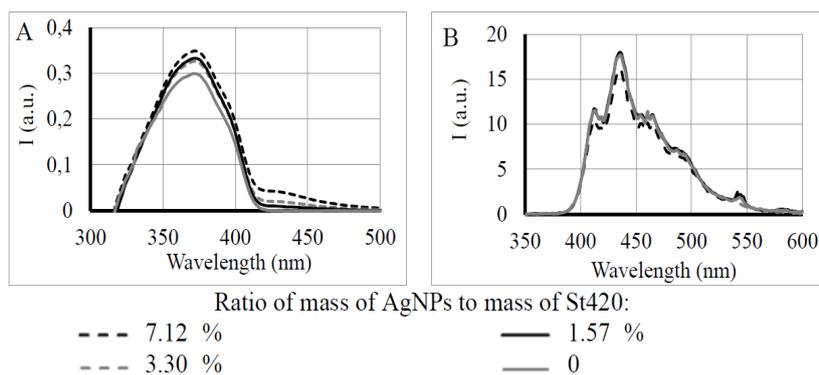- - - 7.12 %   —— 1.57 %
- - - 3.30 %   —— 0

Figure 3. Spectra of absorption (A) and fluorescence (B) of PVA samples containing St420 and AgNPs.
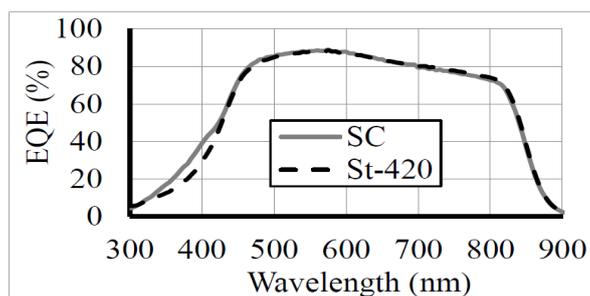

Figure 4. EQE of SC and SC with DS containing St420.

As one can see from Figure 4 the presence of DS containing St-420 also leads to decrease of EQE in the range (300–450) nm. In this case the decrease of EQE value is larger than in case of BBQ dye. Table 3 demonstrates some enhancement of efficiency of SC with increase of concentration of St420 in DS.

Table 3.
Volt-ampere characteristics of the SC coated with polymer films with St420.
*Relative efficiency is calculated from the efficiency of the SC, which is assumed to be equal to 100%.

Sample	Jsc, mA/cm^2	Pmax, mB/cm^2	Efficiency, %	Relative efficiency*, %
SC	-23.60	-11.10	11.10	100
0.15%	-23.36	-11.00	11.00	99.10
0.30%	-23.36	-10.94	10.94	98.56
0.59%	-23.62	-11.11	11.11	100.05
1.19%	-23.62	-11.12	11.12	100.23

For mass concentration of St-420 in a film of 1.19% some increase of efficiency of SC by 0.23%. But this fact contradicts to data presented in Figure 4, which suggest that efficiency should decrease with increase of St-420 concentration. This contradiction could be explained by different principles of work of the devices for measuring EQE and VAC.

The device for measuring EQE detects radiation energy incidenting on SC at some wavelength and energy generated by SC under illumination by the same light Next the device calculates quantum efficiency as a ratio of energy generated by SC to incident on SC energy. Thus, the shape of incident light does not effect on value of EQE.

The device for measuring I-V parameters of SC is irradiated by the light resembling solar light. This device measures basic parameters of SC, which directly depend on spectra and intensity of incident light.

Figure 5 demonstrates spectrum of light emitted by solar simulator as well as calculated on the basis of EQE of SC spectrum of effective absorption of SC.
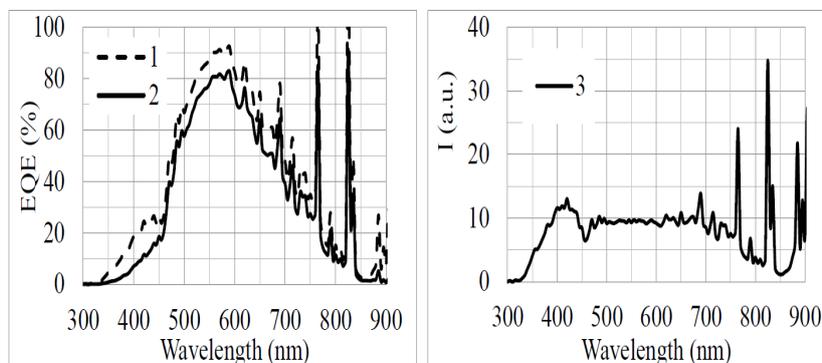

Figure 5. Spectrum of emission of solar light simulator (1), calculated based on EQE spectrum of effective absorption of SC (2) and difference of spectra 1 and 2 (3).

Figure 5 shows that in the range of (300-400) nm effective absorption of SC is negligible since solar light has small emission intensity in this range and there is small value of EQE in this spectral range. Since dye St420 has absorption in the range 350 - 400 nm then it almost does not compete for absorption with SC. If one subtracts from curve 1 curve 2 in Figure 5 then one may obtain curve 3, which describes energy lost by SC. Obviously, significant amount of energy is lost in the range (350-400) nm. The dye St420 collects this lost energy and re-emits it the range of (400–500) nm, where efficiency of SC is much higher. Therefore, we observe some increase of efficiency of SC (covered by DS containing St420) according to results of VAC, and at the same time decrease of EQE value is observed.

Conclusion

Based on the obtained results we can make following conclusions:

1) There is some competition between DS and SC for solar radiation due to the fact that some part of energy absorbed by DS does not transmitted to SC;

2) Larger amount of energy is lost due to absorption by DS than energy re-emited;

3) AgNPs quench emission of St420 in PVA film;

4) Spectral range of absorption is more important parameter than spectral range of fluorescence of DS applied for SC;

5) Increase of efficiency of SC using DS could be achieved using St420 even if the EQE curve of DS demonstrates some decrease.

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