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DYE PHOTOSENSITIZERS AND THEIR INFLUENCE ON DSSC EFFICIENCY: A REVIEW

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Abstract. *Since early 1990s dye-sensitized solar cells (DSSC) has been developed by many research groups all over the World. This paper presents a review of researches focusing on photosensitizer influence on DSSC efficiency. Variety of dye substance has been analyzed. The highest efficiency around 11.2% has been noted for ruthenium-based DSSC devices. Natural dyes allowed to reach 4.6%. The most metal-free organic dyes resulted in efficiency ranged from 5% to 9%, however, some of them (e.g. Y123) allowed to obtain devices with efficiencies equal to 10.3%. Co-sensitization is the new approach which results in efficiencies up to 14.3%.*

Keywords: photovoltaic cells, renewable energy sources, energy conversion, DSSC

SUBSTANCJE SENSYBILIZUJĄCE I ICH WPŁYW NA SPRAWNOŚĆ BARWNIKOWYCH OGNIW SŁONECZNYCH (DSSC): PRZEGLĄD

Streszczenie. *Od początku lat 90 XX wieku ogniwa barwnikowe przyciągają uwagę naukowców na całym świecie. Praca ta poświęcona jest przeglądowi badań dotyczących wpływowi substancji sensybilizujących na sprawność barwnikowych ogniw słonecznych (DSSC). Największą sprawność uzyskują ogniwa sensybilizowane barwnikami na bazie rutenu, podczas gdy barwniki naturalne pozwalają na pracę z wydajnością 4,6%. Sprawność konwersji energii ogniw uczulanych barwnikami organicznymi wynosi 5-9%, jednakże niektóre z nich, np. Y123 pozwalają na uzyskanie wydajności rzędu 10,3%. Zastosowanie kilku barwników do sensybilizacji jest nowym podejściem, które przekłada się na wartości sprawności nawet do 14,3%.*

Słowa kluczowe: ogniwa fotowoltaiczne, odnawialne źródła energii, konwersja energii, barwnikowe ogniwa słoneczne (DSSC)

1. Introduction

Nowadays renewable energy sources are becoming more important due to the intense development of society combined with the depletion of fossil fuels. It should be noticed that energy demand is still increasing. One of the reasons is a tremendously growing population and significant improvement of its living standard. Another reason is the industry enhancement. Electricity is a core resource for the development of human civilizations. It is anticipated that power demand increases by 90% from today to 2040, because of the use of electric mobility, heating, and common electricity access [46, 55]. However, the current scheme of supply and use of energy is unsustainable and it should be stabilized in the short-time perspective. What is more, global warming and the climate change force the present generation to search environmentally friendly energy technologies which will contribute to sustainable development for the subsequent generations. Electricity can be received from various resources such as coal, natural gas or biomass. It should be taken into account that fossil fuels combustion has a tremendous impact on the environment. Environment preservation during the energy production process is crucial. Therefore, the energy production method should be reoriented towards renewable resources. Greenhouse gases emission, such as CO_2, SO_X, NO_X, to the atmosphere is limited by Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources which assumes the emission reduction. What is more, European Council has presented a variety of legislative proposals related to the reform of the EU energy market called "Clean Energy for All Europeans". On the basis of these documents, Poland should achieve 32% of renewable energy sources in final energy consumption by the end of 2030 [54]. The renewable energy sources are characterized by high temporal and spatial variability thus they need to be carefully balanced and used in the national energy plan in order to maintain a well-balanced supply. Solar photovoltaic technology has tremendous high potential energy contribution which can fulfil the energy demands of the entire world. Therefore, and having regard to this fact, harvesting and supplying photovoltaic (PV) technologies should be readily available [7]. Photovoltaic use the direct conversion technology of sunlight into high-quality electricity energy. Three main categories of photovoltaic solar cells, called generation, can be distinguished. Currently, the market is covered by the first two. The most-known, the first generation is based on crystalline silicon material. The silicon wafers production and environmental costs are relatively high, but this technology is the most effective one. The research group of Yoshikawa [50] achieved efficiency equals 26.7%. The second generation of solar cells, which is called thin-film technology, is mainly based on cadmium sulfide (CdS), cadmium telluride (CdTe), amorphous silicon (a-Si) and copper-indium-diselenide/copper-indium-gallium-diselenide (CIS/CIGS). P. Jackson et al. [18] produced CIGS laboratory solar cell with the highest efficiency of 22.4%. It has created the opportunity to replaced high-cost conventional silicon solar cells with CIGS ones. However, the type of solar cells which focuses the attention of research groups all over the world are dye-sensitized solar cells (DSSC). They belong to the third generation of photovoltaic cells which is classified as a cost-effective photovoltaic device mainly due to inexpensive materials and simple fabrication process. After the breakthrough, in 1991, made by the group of Gratzel [32], DSSC are considered as one of the most potential renewable power sources. In contrast to conventional solar cells based on the p-n junction made of semiconductor, DSSC consist of four main components:

1) photoanode, called working electrode, with a mesoporous semiconductor layer (mostly made up of titanium dioxide (TiO_2));
2) counter electrode covered by a catalyst which is typically platinum;
3) electrolyte containing the redox couple; its main role is to collect electrons at the counter electrode and dye sensitizer-regenerating;
4) dye sensitizer absorbed on the TiO_2 molecules.

The scheme of dye-sensitized solar cells is presented in Fig. 1.

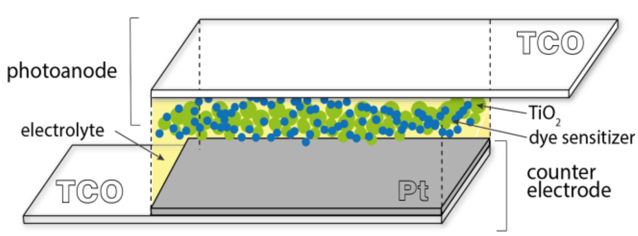

Fig. 1. Scheme of dye-sensitized solar cells

Dye-sensitizer solar cells are photoelectrochemical devices which use an electrolyte as the charge transport medium. Both electrodes are based on transparent conductive oxide (TCO) substrates. They are covered by several microns thick of mesoporous and nanostructured indium tin oxide (ITO) [38] or fluorine-doped tin oxide (FTO) [26]. In the process of manufacturing the DSSC, FTO material is more common, because is high temperature resistant which is important since the working electrode covered with TCO and semiconductor needs annealing treatment. At relatively high temperature degradation of electrical properties of ITO layers can appear, whilst layer based on fluorine-doped tin oxide is much more stable. ITO is characterized by the highest available optical transmittance of ~90% in visible spectrum light with the lowest electrical resistivity of $\sim 10^{-4}\ \Omega\cdot$cm [28]. Among all the components, the dye plays a crucial role in the conversion of sunlight into electricity [1, 19]. Its role is to extend the absorption of solar light by mesoporous TiO_2 layer from visible to the near-infrared range (up to 920 nm) in the solar spectrum and thus increasing the efficiency of solar conversion [10]. It should be pointed out that DSSC use electron transfer reactions in a molecular scale. The initial efficiency that achieved by Gratzel equals 7% in 1991 [32], then it raised up to the value of 10% in 1993. Nowadays, the most efficient DSSC device works with an efficiency of 13% [30]. The attention on many research groups is focused on clarification of DSSC working principles, improvement of conversion efficiency, and commercialization.

Dye-sensitized solar cells have many components that have to be optimized not only as an individual but also as a part of the highly-advanced assembly. The efficiency of working cells absolutely depends on the type of substance used as dye sensitizer. This review article aims to represent recent studies of dyes that have provided important pathways towards better device performance.

2.1. Dye sensitizer

The efficiency of dye-sensitized solar cells is strongly determined by the molecular structure of the photosensitizer [43]. Roslan et al. [34] divided the photosensitizers into three groups: metal-complex, organic and natural photosensitizer. However, some research groups, such as [3, 17, 24] distinguish into natural and synthetic substances (metal complex dyes and metal-free organic dyes). The group of synthetic sensitizers is represented by e.g. polyphyridal complexes of ruthenium and osmium, metal porphyrin, whereas organic one includes natural and synthetic substances. However, the principal criteria that are taking into account are an environmental influence, manufacturing, and origin of the dyes, ability of absorbance the wide spectra of the light and durability. The whole surface of the nanoparticles titanium dioxide should be covered with a single layer of molecules' dye which causes the effective electron injective into the semiconductor material directly. It would be low effective or even impossible if it was realized through the few layers of sensitizer.

What is more, an ideal dye sensitizer should fulfil important requirements, which are as follows [12, 49, 52]:

1) wide absorption spectrum; maximum photons harvesting from visible to the near-infrared region;
2) production of photo-excited electrons;
3) the ability of effective charge infusion into the conduction band of the mesoporous semiconductor layer;
4) appropriate levels of LUMO and HOMO providing effective electrons injection;
5) ability to dye regeneration; the oxidation potential of dye should be higher than the oxidation potential of redox couple contained in an electrolyte;
6) presence of chemical groups that are capable of permanent chemisorption of photosensitizer onto the TiO_2 surface, such as $-COOH$, $-H_2PO_3$, $-SO_3H$;
7) thermal and chemical stability, good solubility.

Metal complex dyes that have been widely investigated are based on ruthenium (Ru), iridium (Ir), osmium (Os). These elements are considered as heavy metals; complexes which they create are characterized by a long excited lifetime, high efficiency of DSSC assembly, and high redox properties.

2.2. Ruthenium (Ru) complex photosensitizers

Nowadays, the DSCC assemblies that occur the best efficiency are ruthenium-based. They are characterized by high efficiency, excellent chemical stability, and absorption of solar radiation in a wide range. Researchers developed many sensitizers based on ruthenium element. Among them, the most well-known and widely used are N3 ("red" dye), N749 ("black" dye), N719, Z907 complexes. N719 and N3 photosensitizers have almost the same structure; in the molecule of N3 is TBA^+ instead of H^+ at two carboxyl groups. The red and black dyes are often used as indicator ones. Many researchers [5, 11, 25] are working on N719-based dye-sensitized solar cell assemblies, but the highest efficiency equals 11.18% was obtained by [14]. The most important thing during the optimization of the photosensitizer for solar cells applications is the ratio of electrons injection rates and recombination (reverse and forward electron transport) [13]. High efficiency of the N3 and N719 dye is the result that the injection process is much faster than recombination due to the separation of the donor LUMO orbital and the acceptor HOMO. However, all of Ru-based DSSC obtain similar, excellent efficiency on the level of 10-11%, which is shown in Table 1. That is caused especially by wide absorption range from visible to near-IR light. In the last years, in the field of dye-sensitized assemblies based on ruthenium, the stagnation can be observed. It is caused by a disadvantageous impact on the environment by their chemical nature. In addition, the synthesis of ruthenium complexes is a sophisticated and expensive procedure, and these complexes have a strong tendency to degrade in the water environment [51].

Table 1. The efficiency of the Ru-based dye-sensitized solar cells

Dye	Full name	η [%]	Ref.
N3	cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)	10.00	[48]
N719	di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)	11.18	[14]
N749	tris(N,N,N-tributyl-1-butanaminium)[[2,2″6′,2″-terpyridine]-4,4′,4″-tricarboxylato(3-)-N1,N1′,N1″]tris(thiocyanato-N)hydrogen ruthenate	10.40	[33]
Z907	cis-Bis(isothiocyanato)(2,2′-bipyridyl-4,4′-dicarboxylato)(4,4′-di-nonyl-2′ bipyridyl)ruthenium(II)	11.10	[6]

Mathew et al. [30] achieved high conversion efficiency for the metal complex-based dyes which was 13% with the following working parameters: open-circuit voltage V_{OC} – 0.91 V, short-circuit current density J_{SC} – 18.1 mA/cm^2, fill factor FF – 78%.

2.3. Natural dyes

Natural dyes have received intense research interest in recent years. They are considered as promising photosensitizers in dye-sensitized solar cells field because of low cost, resource reproducibility, non-toxic environmental impact, and their abundance of prevalence. The biggest advantage of dyes based on natural substances is that they are never threatened with extinction, even with very high usage. Pigments in natural dyes can be easily extracted from flowers, leaves, and fruits of some plants [9]. Each part of the natural plant is characterized by different pigment colour. What is more, obtaining natural dyes and optimization of extraction methods are less sophisticated than in case of ruthenium complexes, and thus the negative impact on the natural environment can be easily reduced [4].

Natural sensitizers are characterized by absorption in the range 400–700 nm (visible region range) [23, 31]. Natural dyes present widely spectrum of colours from light yellow to dark brown. These substances are often used for educational purposes in order to evaluate which type of dyes are suitable for sensitization. Among them, the most investigated are chlorophyll, anthocyanin, carotenoids, flavonoids.

Chlorophyll and anthocyanin will be described as a representative dyes of this group of photosensitizers.

2.3.1 Chlorophyll

Chlorophyll is one of the most abundant dye. It occurs in almost all plants and is characterized by green colour (it is called "natural green dye"). Chlorophyll can be easily extracted, especially from leaves. This dye can absorb the light from red, blue and violet wavelengths. The strong absorption peaks can be observed at 430 nm and 660 nm [40]. The very first research about chlorophyll as a photosensitizer was published in 1972 by Tributsch [44]. The structure of the chlorophyll dye is presented in Fig. 2.

Taya et al. [41] presented the research in which chlorophyll was extracted from *anethum graveolens, parsley, arugula, spinach oleracea,* and green algae. It was shown that the condition of the basic material matters. Fresh or dried leaves from plants mentioned above affect strongly the adsorption of chlorophyll onto the photoanode surface and consequently the performance. This research group obtained results before and after drying and the best efficiency was obtained for DSSC assembly sensitized by the *spinach oleracea* with drying process implemented equals 0.29%.

The dye-sensitized solar cells can be also sensitized by chlorophyll extracted from fig leaves. The highest energy conversion efficiency obtained with the fig leaves was reported at [42] and it is equal to 0.64%. Also, a dye extracted from cream leaves resulted in good performance of the DSSC (0.607%).

The research group of Kabir et al. [20] reported stability study of natural green dye extracted from spinach leaves *(Spinacia oleracea),* prepared with methanol. They obtained the dye-sensitized chlorophyll-based assemblies with an efficiency of 0.398%. Then the stability test was made which showed the diminishing efficiency to 0.395% after a period of 192 hours. However, the degradation rate deteriorated with time as well.

Wang et al. [47] have extracted chlorophyll dyes from brown seaweed, *U. pinnatifida*. They examined two different types of chlorophyll and their oxidized forms. For each type of c-type chlorophyll, they obtained very high conversion efficiencies up to 3.40% and 4.60% for basic dyes; 2.60% and 2.50% for their oxidized forms.

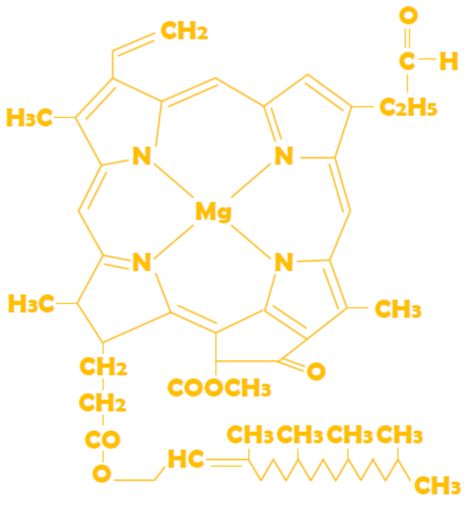

Fig. 2. Basic molecular structure of chlorophyll pigment

2.3.2. Anthocyanin

Anthocyanin is classified as a part of large flavonoids group. The use of anthocyanin in DSCC results in intense red to blue colour. Besides the chlorophyll, it is the most important group of visible plant pigments. Anthocyanins are also well-known due to their excellent antioxidant properties. This natural pigment is characterized by wide absorption in the range of 450–600 nm due to charge transfer transitions from HOMO to LUMO [16]. Big advantage of this dye is the presence of carbonyl and hydroxyl groups in the molecular structure (Fig. 3) which helps in attaching with TiO_2 molecules for good sensitization, and thus good energy conversion efficiency of sensitized assembly. Anthocyanin can be found in a wide group of plants in their leaves, fruits, petals, and roots [39]. Blackberries, grapes, aubergines, mango, blueberries, red onion or red cabbage are the main origin of the anthocyanin dye. The colour of the sensitized TiO_2 matters, darker anthocyanin pigment leads to higher efficiency [36]. Darker colour enhances light absorption and thus caused better conversion energy efficiency.

Adel et al. [2] used anthocyanin dyes extracted from three different plants: blackberry, hibiscus, and rose. They achieved the efficiency of 0.76%, 0.058%, 0.044% for blackberry, hibiscus, and rose dye, respectively with the use of iodine electrolyte.

The research group of Calogero et al. [8] used blackberries, red Sicilian orange and aubergine which resulted in dye-sensitized solar cells worked with the efficiency of 1.15%, 1.01%, and 0.64% respectively. The obtained DSSC worked with the J_{sc}, V_{oc} and *FF* parameters which were equal to 7.68 mA/cm^2, 348 mV and 0.43 respectively.

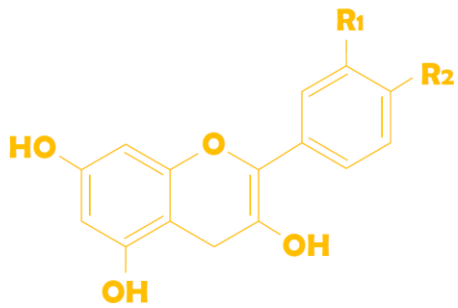

Fig. 3. Basic molecular structure of anthocyanin pigment

However, the anthocyanin dye can be extracted also from pomegranate with high success. In the work of Ghann et al. [15] the efficiency of 2.00% has reported. They observed a strong absorption peak at 510 nm which matches with anthocyanins' absorption range. The dye-sanitized assemblies worked with V_{oc} – 390 mV, J_{sc} – 12.20 mA/cm^2 and FF parameter equal to 0.41.

It should be mentioned that natural an anthocyanin dyes have synthetic derivatives which show promising properties as efficient sensitizers for dye-sensitized solar cells.

2.4. Metal-free organic dyes

Organic dyes used in dye-sensitized solar cells field are characterized by high molar absorption, the wide diversity of molecular structures which enable to model vast variety of dyes, low cost, and flexibility for molecular designing. However, in comparison with metal complexes-based dyes, they obtained lower conversion efficiencies.

The design of organic sensitizers is typically based on the configuration "D-π-A", where D is a hydrophobic electron rich donor, π -bridge, A - hydrophilic electron-deficient acceptor. The acceptor is also a structure which anchors the titanium dioxide semiconductor layer. The typical structure is shown in Fig. 4. This structure is also known as the 'push-pull' structure or 'DpA' [27].

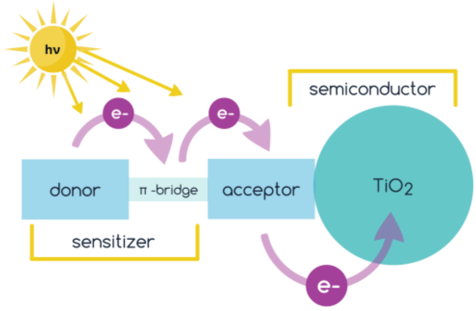

Fig. 4. Scheme of donor- π-acceptor organic dye structure

The main factor which can limit the efficiency of working DSSC sensitized with organic dyes is the occurrence of dye aggregates formation on the surface of TiO_2 nanoparticles which caused suppressing of the excited state of the sensitizer molecules.

It can be distinguished many metal-free organic dyes classes which are the subject of investigation. Among them, alizarin, coumarin, cyanine, triphenylamine, carbazole-based sensitizers which obtained the efficiency up to 5–9% [37, 52] can be underlined.

Alizarin is one of the metal-free organic dyes which results in red colour in DSSC. This dye is characterized by rapid injection electrons into the semiconductor conduction band with the indirect mechanism. The dye has wide absorption (400–600 nm) with the strongest peak at 432.5 nm [22]. The molecular structure of alizarin is shown in Fig. 5.

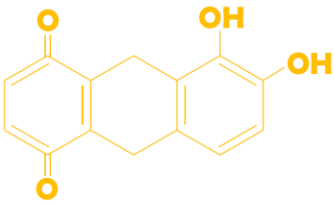

Fig 5. Basic molecular structure of alizarin pigment

In the paper by [35], the working parameters of alizarin-based DSSC with four different redox couple electrolytes e.g. (KI), $[(CH_3)_4NI]$, $[(CH_3CH_2)_4NI]$ and $[(CH_3CH_2CH_2)_4NI]$ were examined. They achieved the dye-sensitized assemblies worked with the efficiency of 0.635%, 0.383%, 0.78%, and 0.915%.

Whereas, the research group of Manmeeta [29] fabricated two types of assemblies: $TiCl_4$ treated and untreated TiO_2 material with the use of oxidized alizarin photosensitizer. In the first group, they obtained J_{SC}, V_{OC}, FF and efficiency parameter equals to 9 mA/cm^2, 750 mV, 0.53 and 3.57% respectively. However, the research has shown that $TiCl_4$ treatment significantly improves all working parameters, especially energy conversion efficiency (5.12%).

Tsao et al. [45] reported the power conversion efficiency of 10.3% by use of organic dye (Y123) and cobalt base electrolyte. Nevertheless, a very good effect can be observed by co-sensitization with two metal-free organic sensitizers. Kakiage et al. [21] demonstrated sensitized DSSC with ADEKA-1 and a carboxy-anchor organic dye of LEG4 collaboratively which show an excellent record of efficiency, up to 14.30%.

3. Conclusion

Dye-sensitized solar cells are a generation of photovoltaic devices which is intense explored and thus developed over the three decades. However, still many components need to be improved in order to enhance working parameters (V_{OC}, I_{SC}, J_{SC}, FF) and efficiency of DSSC assemblies. Dyes presented in this review article are only a small part of a broad group of photosensitizers. Molecular structure of dyes can be easily modified which resulted in nearly infinite types of photosensitizers. Nevertheless, there is a strong need for high-performance dyes which increase light adsorption by the semiconductor material. The very high efficiencies are obtained by ruthenium-based dye-sensitized solar cells by now (up to 11%), however, they should be replaced with metal-free dyes with the nontoxic influence of environment. Natural dyes extracted from plants seem to be a promising alternative as well as organic dyes with efficiencies reaching 9%. However, it should be clarified that not only the photosensitizer but also other components and their mutual adjustment is of high importance. Wherefore, a new approach to co-sensitization results in the value of efficiencies which can be compared with those for Ru sensitizers. The comprehensive discussion allows to suggest that utilization of natural and metal-free dyes in DSSC result in high performances in the foreseeable future.

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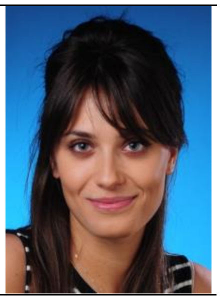

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