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Approaches to Improve Efficiency of Dye-Sensitized Solar Cells

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Questions related to energy development became more and more important every year. Solar radiation is about inexhaustible, environmentally friendly and available source of energy. One of the directions of photonics is to create dye-sensitized solar cells (DSSC), also called Grätzel cells. To date, DSSC efficiency reaches 13%. In addition, they have several advantages: they are made of cheap and environmentally friendly materials and do not require sophisticated equipment to manufacture. Research aimed at improving the efficiency of DSSC does not stop. The main ways of increasing the efficiency are: the selection and modification of the dye used; using of different types of semiconductor nanoparticles and their modification; variation in the method of dye binding to the semiconductor nanoparticles; use of co-adsorbents and co-sensitizers when applying dye; iodide electrolyte replacement, including solid- and gel-type electrolytes. This review focuses on modern advances and research in these areas.

Keywords: Dye-sensitized solar cells (DSSC), Grätzel cells, photocurrent, photoelectrochemistry, photoconvertion efficiency.

Подходы к повышению эффективности сенсибилизированных красителем солнечных ячеек

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С каждым годом все большую актуальность приобретают вопросы, связанные с развитием энергетики. Солнечное излучение является практически неисчерпаемым и экологически чистым доступным источником энергии. Одним из направлений фотоники является создание солнечных ячеек, сенсибилизированных красителем (DSSC), также называемых ячейками Гретцеля. На сегодняшний день эффективность DSSC достигает 13%. Кроме того, они обладают рядом преимуществ: изготавливаются из дешёвых и экологически чистых материалов и не требуют сложной аппаратуры при производстве. Не прекращаются исследования, направленные на повышение эффективности DSSC. К основным путям повышения эффективности можно отнести: выбор и модификация используемого красителя; использование полупроводниковых наночастиц различных типов и их модификация; варьирование способа связывания красителя с полупроводниковыми наночастицами; использование ко-адсорбентов и ко-сенсибилизаторов при нанесении красителя; замена йодсодержащего электролита, в том числе на твердые и гелеобразные электролиты. Настоящий обзор посвящен современным достижениям и исследованиям по данным направлениям.

Ключевые слова: Сенсибилизированные красителем солнечные ячейки, ячейки Гретцеля, фототок, фотоэлектрохимия, эффективность фотоэлектропреобразования.

Introduction

Questions related to energy development become more and more important every year. The problem is to ensure energy consumption by constantly growing world population without consequences for the environment, which may eventually become insurmountable. The solution of this problem can be found through the use of alternative energy sources. Today, most of renewable energy sources are characterized by a limited capacity or by the difficulty of their development, which calls into question their usefulness in economic terms. As an alternative, the solar radiation is practically inexhaustible, environmentally friendly and available source of energy. Numerous studies in the field of solar energy have shown that in the near future, this method of producing energy can be economically viable and widely used.^[1] Bet on solar energy should be seen not only as a win-win, but in the long run as the uncontested choice for humanity.^[2]

In this regard, one of the modern areas of photonics is the imitation of natural photosynthetic structures in which a photoinduced energy and electron transfer processes occur, with a view to build effective light-energy-harvesting devices. Light-harvesting solar cells based on biomimetic principle can serve as an alternative to semiconductor cells to generate energy.^[3-7]

Modern dye-sensitized solar cells (DSSC), also called Grätzel cells, were invented by Brian O'Regan and Michael Grätzel in 1991.^[8] Schematic representation of the dyesensitized solar cell is shown in Figure 1.



Figure 1. Schematic representation of DSSC with the energy levels shown.

Titanium dioxide nanoparticles were deposited on the electrode, and then were covered with a layer of lightabsorbing dye.

Under the influence of light the transition of the dye into an excited state and electron transfer in conduction band of a semiconductor (titanium dioxide) occur. An electrode and a counter electrode are placed in the electrolyte containing a redox couple which was iodide/triiodide pair. Ruthenium complex 1 with a strong absorption in the visible region of the spectrum has been selected as a dye.



In this case, the overall efficiency of converting light energy into electrical energy was 7.1–7.9 %. The main difference from the semiconductor solar cells was the division of the light absorption and charge transport functions of Media. Subsequently, in 2010, for this invention Grätzel was awarded Millennium Technology Prize.^[9]

This review describes the current state of this field of photonics and the main ways of DCCS modification in order to increase their efficiency. It contains mainly the recent progress about scientific results. In this case the active cells areas are small (between 0.1 and 0.5 cm²) which is not useful for practical applications yet without successful up-scaling.

The DSSC Efficiency: Current Achievements and Future Prospects

A summary table for maximum efficiency and other relevant characteristics of the different type light-converting devices is published every six months in the journal Progress in Photovoltaics: Research and Applications. ^[10] Dye-sensitized solar cell to date has shown maximum power conversion efficiency 11.9 %. Although this result looks quite modest in comparison with classic silicon solar cells whose efficiency reaches 25 %, DSSC have a number of indisputable advantages. Solar panels of this type are much more promising, as are made of cheap and environmentally friendly materials and do not require sophisticated equipment to manufacture. These cells have a simple structure, sufficiently resistant to temperature changes, effectively absorb solar radiation at different angles of incidence, they are durable and easy to operate. In addition, it should also be borne in mind that the abovementioned reporting table includes only experimental data, confirmed by independent test centers, and they possibly do not reflect the latest achievements of scientific groups working in this area.

Calculation of DSSC Efficiency

Efficiency η of photovoltaic cells depends on such parameters as open-circuit voltage ($V_{\rm OC}$), short-circuit current ($I_{\rm SC}$), fill factor (FF) and the luminous power taking into account the area of the solar cell surface (P_{η}).^[11]

Fill factor FF is calculated using the formula (1):

$$FF = \frac{V_m \cdot I_m}{V_{OC} \cdot I_{SC}}$$
(1)

where $V_{\rm m}$ – cell voltage at which the maximum power is reached, $I_{\rm m}$ – cell current at which the maximum power is reached, $V_{\rm OC}$ – open-circuit voltage, $I_{\rm SC}$ – short-circuit current. The efficiency of the solar cell is calculated using the formula (2):

$$\eta = \frac{V_{OC} \cdot I_{SC} \cdot FF}{P_L} \tag{2}$$

Thus, to determine the solar cell parameters it is necessary to establish its current-voltage characteristics (I-V curve) and the generated power curve.

Table 1 represents few examples of different DSSCs to show their characteristic parameters orders.

Table 1. Parameters of examplarily DSSCs.

Dye	SM315 ^[47]	XW-11+WS-5 ^[86]	N749 ^[111]
$V_{\rm oc}, {\rm mV}$	910	760	720
$I_{\rm SC}$, mA/cm ²	18.1	20.3	20.5
FF	0.78	0.74	0.70
$P_{\rm L}$, cm ²	0.159	0.120	0.186
η, %	13.0	11.5	10.4

Another graphical characteristic is an incident photonto-electron conversion efficiency (IPCE), which is usually represented as a function of wavelength. IPCE is the external quantum efficiency of solar cells and largely depends on the characteristics of the light-absorbing dye used. Sometimes absorbed photon conversion efficiency (APCE) also provided, which is the internal quantum efficiency and does not depend on the light absorption by a dye.

As it follows from the analysis of numerous data in the literature, to improve the efficiency and to optimize some other parameters of DCCS, various research groups offer following approaches:

- selection and modification of dye used, which affect the absorption of light and electron transfer to the semiconductor;
- use of any type of semiconductor nanoparticles and their modification;
- variation in the method of dye binding to the semiconductor nanoparticles;
- use of co-adsorbents and co-sensitizers when applying dye;
- replacing the iodide-containing electrolyte, especially by solid and gel-type electrolytes, *etc*.

This review demonstrates these approaches to modifying DSSC.

Types of Dyes for DSSC and Modern Approaches to Their Molecular Design

The dye is the central element of DSSC, which absorbs light. Therefore, the choice of dye may have the greatest

impact on the overall efficiency of the cell. Perfect dye should possess the following properties:

- 1. The dye should absorb light across the visible and near-IR region.
- 2. The dye should have anchoring functional group (-COOH, -PO₃H₂, -SO₃H, *etc.*) for interaction with the semiconductor surface.
- 3. The highest occupied molecular orbital (HOMO) should be placed as far away as possible from the conduction band of the semiconductor particles. Wherein the HOMO energy must be considerably lower than that of the redox couple in the electrolyte.
- 4. The lowest unoccupied molecular orbital (LUMO) must be as close as possible to the semiconductor surface, preferably in an anchor group. LUMO energy of the dye must be considerably higher than the potential of the conduction band of the semiconductor.
- 5. The dye should have fluorescent properties.
- Lateral dye substituents should be hydrophobic to minimize contact of electrolyte and photoanode, which may cause elution of the dye from the surface of the anode, thereby reducing the lifetime of the cell.
- 7. The dye molecules should not be aggregated on the surface of semiconductor particles.
- The dye must have a photo, thermal, chemical and electrochemical stability, and must be stable under prolonged exposure to sunlight and in an electrolyte medium.

Existing dyes can be divided into several groups. The first group includes metal-containing dyes, among which the most widely used ruthenium complexes. The second group consists of very numerous organic dyes with a variety of structures, but not containing metal. The third group includes tetrapyrrol macroheterocycles such as porphyrins and phthalocyanines. Often these compounds are used in the form of metal complex and an organic part of the molecule makes it easy to carry out chemical modification of these compounds by introducing functional groups, expanding π -conjugation and producing various conjugates. Further uniqueness of these compounds is that tetrapyrrolic rings act as light-harvesting antennae in the natural process of photosynthesis, and the creation of light-harvesting devices from these heterocycles can be attributed to biomimetic. It should be noted that there are more detailed classification of dyes.

Dyes Based on Ruthenium and Other Metals

Ru(II) complexes proposed by Grätzel were one of the first type of dyes used in DSSC.^[8] Such dyes are still attracting the attention of many scientific groups, as they have excellent photoelectrochemical properties, allowing to achieve record results photocells efficiency.^[12] Pyridinethiocyanate ruthenium complexes with different substituents in pyridine are the most widely used, particularly dyes **2** (N3), **3** (N719), **4** (N749, Black dye). However, one of the factors hindering the widespread use of dyes based on ruthenium is their high cost.

Currently, there are many attempts to create a DSSC based on other metal complexes, in particular osmium,^[13] rhenium,^[14] iron,^[15] platinum,^[16] copper.^[17]



Organic Dyes

Organic dyes consist even of more numerous groups. Compared with ruthenium complexes they are less expensive, more environmentally friendly and usually have higher extinction coefficients. These molecules may also be modified relatively easily, which allows changing the levels of HOMO and LUMO, shift or broaden the absorption region.^[18] The results of modern research of photovoltaic properties of the most common classes of organic dyes are shown below, among which – dyes based on coumarin, triarylamine, carbazole, indoline, cyanine, squaraine, oligothiophen, phthalocyanine, porphyrin, *etc.*

The dependence of the efficiency of photovoltaic cell structure and intramolecular charge transfer in a dye based on 7-(dialkylamino)coumarin-3-carboxylic acid was investigated in the study.^[19] In the dye **5** rotation around nitrogen-coumarin bond is impossible while in the dye **6** rotation around this bond in the excited state prevents unwanted recombination process that has allowed to achieve better results with dye **6**.



Authors^[20] have studied the number of donor- π -acceptor type dyes based on triphenylamine with one, two and three acceptor substituents on which the anchor group was located; wherein the dye with two anchor groups showed the highest efficiency. It was carried out quantum-chemical calculation of properties of some donor- π -acceptor type dyes based on triarylamine with various π -conjugated spacers and various acceptors. Eight of the compounds have shown promising results for use in DSSC.^[21]

Paper ^[22] is dedicated to the dye on the basis of triarylamine with alkoxyl substituents, provided decrease in charge recombination on the surface of titanium dioxide and, as a consequence, increasing open circuit voltage. However, the authors pointed out that steric hindrance decreases dye coating of the semiconductor surface, which reduces the short-circuit current. Paper ^[23] illustrates the synthesis of

5,7-dihydro[2,3-*b*]carbazole, and synthesis of similar dye with two anchor groups. Authors have studied the structure of the dye on the surface of titanium dioxide, dye molecules were C-shaped. Photovoltaic cell parameters were studied, the effectiveness was 6.02 %.



Crown ether substituted carbazole dye 7 was synthesized and its effect on the concentration of lithium and iodine ions on TiO2/dye/electrolyte interfaces and on the lifetime of the electron and the potential of the conduction band of the semiconductor in comparison with unsubstituted carbazole dye **8** was studied.^[24] Studies have shown that lithium ions coordinated by crown ether attract iodide/triiodide anions preventing their migration to the surface of the titanium dioxide.

A number of dyes based on benzo[a] carbazole with furan, thiophene and oligothiophene substituents were synthesized and their photoelectrochemical properties were investigated. The cells with oligothiophene-substituted dye have shown the highest efficiency, comparable with the standard ruthenium dye N719.^[25]

Study^[26] is dedicated to comparison of coumarin, carbazole and triphenylamine as the donor dye moiety in cells with cobalt complexes as redox couple (Figure 2). Triphenylamine-based dye provided the highest open-circuit voltage, which the authors attribute to blocking effect of large phenyl groups, which prevent contact of cobalt complexes with the surface of the titanium dioxide. Coumarin dye pro-



Figure 2. Studied in^[26] dyes with different donor substituents. Reprinted with permission from Murakami T.N., Koumura N., Kimura M., Mori S. *Langmuir* 2014, *30*, 2274–2279. Copyright 2014, American Chemical Society.

vided the least value of $V_{\rm OC}$, but due to effective light absorption – the highest value of $I_{\rm SC}$ and a bit higher total efficiency.

Processes of ultra-fast twisting of the indoline donor unit were studied,[27] and reflected the impact of such processes on the cell parameters. The authors of [28] studied features of the application of bidentate cyanine dyes on titanium film, their ability to form aggregates, and also developed a model that allows to predict the compatibility of the bidentate dyes with semiconductor surface depending on their crystallographic properties. Squaraine-triarylamine conjugate-based dyes with one or two anchor groups were synthesized and investigated.[29] Introduction of additional anchor group provided a significant increase in efficiency. In the paper [30] authors presented a synthesis of the multichromophoric conjugate squaraine/perylene monoimide/naphthalene diimide (Figure 3), absorbing a wide range of wavelengths. Photoelectrochemical properties of synthesized compounds and DSSC parameters with NiO

semiconductor were investigated. The authors conclude that the creation of multichromophoric structures in which one of the chromophores simultaneously possesses acceptor and light-harvesting properties, is one of the approaches to improve the efficiency of DSSC.

Squaraine dyes with different π -spacers and different anchor groups (phosphoric and carboxylic acid) were synthesized and investigated;^[31] the best performance (8.9 %) has shown the dye with a carboxylic anchoring group and 4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*']dithiophene π -bridge. Synthesis of alkyl substituted oligothiophenes with three to six thiophene units and phosphate anchoring groups is presented in ^[32]; highest DSSC efficiency of about 5 % was achieved using (sexithiophene)phosphonate. Paper ^[33] concerns to a synthesis of alkyl substituted oligothiophenes conjugated to *N*-ethylcarbazole. The effect of various alkyl substituents on the charge recombination rate and efficiency of DSSC was investigated. The DSSC efficiency dependence



Figure 3. Electron transfer in a cell with squaraine and multichromoforic dye.^[30] Reprinted with permission from Warnan J., Gardner J., Le Pleux L., Petersson J., Pellegrin Y., Blart E., Hammarström L., Odobel F. *J. Phys. Chem. C* **2014**, *118*, 103–113. Copyright 2014, American Chemical Society.

Approaches to Improve DSSC Efficiency

of the thiophene units number in the hexyl substituted oligothiophenes was investigated;^[34] the authors concluded that the optimum is three to four thiophene units.

Porphyrins, Phthalocyanines and Their Metal Complexes

Porphyrins and phthalocyanines occupy a special place among organic dyes. Porphyrins are an important part of the natural photosynthetic systems, due to which they are widely used in artificial photosynthetic systems.^[35] Due to the effectiveness of energy transfer processes and electron transport in natural light-harvesting systems porphyrins and their analogs are commonly used in photovoltaic devices.^[36] These compounds are used as dyes for DSSC both in freebase form and in the form of metal complexes. However, unlike ruthenium dyes, more available zinc is often used. Another difference of the porphyrins and phthalocyanines metal complexes is a significant impact of an organic part on the photoelectrochemical properties including light-harvesting properties.

Phthalocyanines with different positions of the anchor carboxyl groups and one sterically hindered phthalocyanine were synthesized, the aggregation dependence of dye structure and influence of aggregation on the efficiencyof DSSC was investigated.^[37] Position of the anchoring group (*para-* for **9**; *meta-* for **10**, *ortho-* for **11**) changes the position of the phthalocyanine cycle relative to the surface of titanium dioxide from perpendicular to almost parallel (Figure 4), which slows down the process of recombination, but reduces the overall efficiency of light absorption. At the same time the introduction of bulky substituents in **12** managed to suppress recombination while maintaining sufficient efficiency of light absorption.



Figure 4. Orientation of phthalocyanine molecules depending on the position of the anchoring group and the presence of bulky substituents.^[37] Reprinted with permission from Matsuzaki H., Murakami T.N., Masaki N., Furube A., Kimura M., Mori S. *J. Phys. Chem. C* **2014**, *118*, 17205–17212. Copyright 2014, American Chemical Society.

A systematic analysis of possible optical and electrical losses in the DSSC has been conducted by the example of a silicon phthalocyanine complex.^[38] In the future this will allow focus on addressing the identified deficiencies of cells and increase their overall efficiency.

The hybrid dye on the basis of ruthenium complex of phthalocyanine and substituted triarylamine was synthesized (Figure 5).^[39]

Optical properties, Förster resonance energy transfer (FRET) processes and electron transfer processes were investigated. Due to FRET process and intramolecular electron transfer a significant increase in short-circuit current and in the overall cell efficiency was achieved.

Four bichromophoric porphyrin-squaraine dyes (13-16) were synthesized.^[40] Their use as compared to the corresponding unconjugated squaraine resulted in increased both short-circuit current and open-circuit voltage, and therefore the overall efficiency of DSSC.

A synthesis of several donor- π -acceptor dyes based on zinc porphyrin complex is presented in ^[41]. DSSC prepared with the cobalt complex [Co(bpy)₃]^{2+/3+} as electrolyte have demonstrated 7.8% effectiveness. Paper ^[42] illustrates the synthesis of zinc porphyrin complex bearing three C₂₄-containing amide groups and a carboxyl group on *meso*phenyl substituents which demonstrated greater efficacy compared to the same dye without the lipophilic amide substituents.

Study ^[43] was dedicated to the synthesis of dichromophoric dye bearing carbazole and porphyrin zinc complex. The authors have compared the effectiveness of DSSC using as sensitizer each of the two chromophores separately, their mixture and synthesized conjugate. As well the dependence



Figure 5. Förster resonance energy transfer and electron transfer processes.^[39] Reprinted with permission from Choi H., Cho N., Paek S., Ko J. J. Phys. Chem. C 2014, 118, 16319–16327. Copyright 2014, American Chemical Society.



on the electron lifetime from the dye used and on the dye loading to semiconductor surface was examined. The authors note the dispersion force effect: organic dye attracts ions of the redox couple to the surface of titanium dioxide. In the case of using carbazole conjugated with porphyrin (so carbazole is on a greater distance from the surface of the semi-





conductor) contrary, this interaction prevents contact of the redox couple with the surface of the semiconductor, increasing the electron lifetime.

In paper ^[44] the porphyrins **17-20** with four different spacers were considered in order to study the influence of a spacer on the efficiency of light energy conversion. In particular, the authors compared phenyl (**17**) and thiophene (**18**) groups to study the influence of spacer's electron-donating ability, and thiophenephenyl (**19**) and benzothiadiazolephenyl (**20**) groups to determine whether an electron-deficient or rich aromatic as a spacer extender is more suitable for DSSC. The highest efficiency of 9.5 % was achieved with a short thiophene spacer.

The paper ^[45] gives an overview of achievements in the synthesis of porphyrin dyes. The authors note that the DSSC using porphyrins have achieved efficiency values typical for ruthenium dye. At the same time the porphyrin cycle may be easily modified by various substituents, allowing to tuning of HOMO and LUMO levels. Further efforts are encouraged to focus on the expansion of the area of absorption in the visible and near-IR, inhibiting aggregation of the dye on the semiconductor surface, the optimization of electron transfer and suppression of recombination processes, the introduction of new redox couples and ensuring long-term stability of the dye.

To date, one of the most effective dyes is porphyrin GY50 with di(*p*-alkylphenyl)amine in one *meso*-position and benzothiadiazolephenyl spacer between porphyrin cycle and carboxyl anchoring group.^[46] This dye showed a strong absorption in the entire visible region of the spectrum and allowed to achieve 12.75% cell efficiency. Authors ^[47] reported the synthesis of the dye SM315 (**21**) with very similar to GY50 structure and even higher efficiency of 13%.

One of the current trends in the search for new dyes becomes computational screening, which allows choosing by the calculations the number of best candidates for further synthesis and research, thus allowing saving resources and efforts of scientific groups. For example, the database of 1029 dyes, which are the zinc porphyrin complexes with



various donor substituents and various acceptor anchoring groups, was created.^[48] Computational screening of this group has allowed selecting some optimal structures that can potentially provide high efficiency of DSSC. Also, five well-studied porphyrins were included to the study to demonstrate that calculations correlated well with the experimental data. Paper ^[49] is also dedicated to modeling 5000 porphyrin dye structures, in which metal atoms in the coordination sphere, the axial ligands of metal complexes, peripheral substituents and anchoring groups were varied.

Selection and Modification of Semiconductor Nanoparticles

The use of titanium dioxide nanoparticles with a large specific surface area for the application of the dye has been one of the key success factors of the cells proposed by Grätzel. Paper ^[50] gives an overview of nanomaterials on the basis of TiO₂, a process for their preparation, properties and applications, in particular for the creation of photovoltaic devices. Today DSSCs based on TiO₂ demonstrate the greatest efficiency, and therefore a lot of works in recent years is devoted to optimize the morphology of nanostructured electrode.^[18]

For example, a significant impact of the semiconductor structure on the efficiency of photocells was demonstrated.^[51] The authors proposed the use of hierarchically structured titanium dioxide nanofibers, allowing almost double the efficiency compared with nanoparticles. In study ^[52], the authors were able to increase the efficiency of DSSC by doping TiO₂ with scandium. Paper ^[53] describes the preparation of crystalline TiO_{2-x}N_x and investigation the influence of microstructure on the efficiency of the semiconductor cell. The authors of ^[54] investigated the modification of titanium dioxide by graphene oxide and nitrogen-reduced graphene oxide. The highest efficiency 7.19% was achieved with the cells containing 0.2 wt.% nitrogen-reduced graphene oxide.

Along with the modification of titanium dioxide there are also tryings to use other semiconductor materials, in particular zinc oxide. ZnO has properties similar to TiO₂, and even has a higher electron mobility, however, ZnO is much inferior to TiO₂ for stability.^[18] Nevertheless, its photoelectrochemical properties attracted the attention of many research groups. Review ^[55] focuses on production, properties and modifications of zinc oxide. The paper ^[56] is dedicated to the study of the effectiveness of various nanostructures of zinc, while ^[57] compares TiO₂ and ZnO in the same photocell. Despite the almost identical dye coating of the surface in both cases, DSSC with titanium dioxide showed almost four times superior efficiency.

Various research groups have also studied the use of SnO_2 ,^[58] NiO,^[59] Nb₂O₅,^[60] the mixed oxides such as Zn_2SnO_4 ,^[61] as well as core-shell structure.^[62-64] However, the cells using the titanium dioxide are most effective and as a consequence most often used.

Methods of Dye Binding to the Semiconductor Particles

One of the essential requirements for dyes when creating DSSC, is the presence of an anchoring group capable of strong binding to the surface of TiO_2 nanoparticles or other

semiconductor material used. The carboxyl group is most widely used as an anchoring group, it binds dye to titanium dioxide good enough, and often provides better results than other anchoring groups,^[31] ceteris paribus.

However, dyes with cyanoacrylic acid,^[65] pyridine,^[66,67] phosphonic acid,^[32,68] tetracyanate,^[69] sulfonic acid,^[70,71] boronic acid,^[72] salicylic acid^[73] and other anchoring groups are found in the literature. The different types of anchoring groups, as well as the characteristics of their binding to the polyoxometalates were discussed in the review.^[74] The paper ^[36] is a more targeted review of anchoring groups in the porphyrin dyes.

Some dye binding techniques that do not require presence of anchoring group on sensitizer have been proposed. For example, hafnium and zirconium porphyrin and phthalocyanine complexes were synthesized.^[75] These metals have a high affinity for polyoxometalates, and due to the large size they form metal complexes in which the metal is located out of the plane of the molecular cores, thereby providing binding polyoxometalate – hafnium/zirconium – porphyrin/phthalocyanine.

In the papers ^[76,77] the another dye loading technique has been described. Carboxyl-containing ligands having in its structure nitrogen-containing heterocycle was bound to a semiconductor surface, and nitrogen-containing heterocycle of ligand in his turn was complexed with a zinc atom of zinc porphyrin complex (Figure 6). The authors were also conducted to compare the efficacy of the cells in which binding ligand is varied. The best results were achieved with 4 (imidazol-1-yl)benzoic acid.

Using Co-adsorbents and Co-sensitizers

Co-adsorbents are used in some cases during the application of dye to the surface of the semiconductor material to reduce the charge recombination, and to prevent the dye molecules aggregation. The most common co-adsorbents are derivatives of cholic acid. For example, DSSC based on the new thiophene-substituted bithiazole has been created and efficiency was 1.13 %.^[78] The use of chenodeoxycholic acid (CDCA) **22** when applying the dye allowed to increase efficiency by up to 1.25 %.



Triazoloisoquinoline based small molecule was synthesized and presented as a co-adsorbent compound.^[79] Its influence on the DSSC efficiency was studied using a ruthenium dye N719. Due to the co-adsorbent it is possible to increase cell efficiency from 8.36% to 8.83%. The authors also varied the amount of co-adsorbent: the optimum dye to co-adsorbent ratio was 1:0.25, while higher amounts of coadsorbent led to lower short-circuit current and cell efficiency. In study ^[80] phthalocyanine-coumarin conjugate was synthesized and the influence of co-adsorbent on the efficiency



Figure 6. DSSC scheme with the dye application using the ligand.^[76] Reprinted with permission from Subbaiyan N.K., Wijesinghe C.A., D'Souza F. J. Am. Chem. Soc. **2009**, 131, 14646–14647. Copyright 2009, American Chemical Society.

of the cell was proved. The authors note that in addition to preventing the aggregation of the dye molecules chenodeoxycholic acid reduces the absorption of light, so it is important to select the optimal number of the co-adsorbent. However, with founded optimum concentration of dye (0.3 mM) and co-adsorbent (6.0 mM), 69% increase in the DSSC efficiency was achieved.

The absorption only a certain part of the spectrum is the factor that limits the efficiency of solar energy conversion for

many dyes. Ideally, the dye should absorb throughout visible and near infrared portion of the spectrum. In practice, this range is much narrower. With the aim of its enlargement cosensitizer absorbing in the region not covered by the dye is applied in addition to the dye.

DSSCs based on carbazole substituted porphyrin dyes 23 and 24 were created, they were applied to a semiconductor with organic dye 25 as a co-sensitizer.^[81]

Dye 25 absorbs in the region between the Soret band



and Q-bands of porphyrin dyes. This combination of lightharvesting properties of various dyes allowed to increase the short-circuit current, as well as to achieve increase in opencircuit voltage due to greater lifetime of an electron. The authors noted that to increase the $V_{\rm oc}$, it is important that both dyes provides the same or similar electron lifetime. As a result, 61 % efficiency increase for **23** and 35 % for **24** was achieved due to the co-sensitizer. Thus, the cell efficiency was 7.88 % and 8.14 % respectively.

Two new cadmium complex of formula $[Cd_3(IBA)_3(Cl)_2(HCOO)(H_2O)]_n$ and $\{[Cd_{1.5}(IBA)_3(H_2O)_6]\cdot 3.5H_2O\}_n$, where IBA is 4-(imidazol-1-yl) benzoic acid have been proposed as a co-sensitizer for the ruthenium dye N719.^[82] Due

to compensation of deficit N719 absorption in the UV and blue-violet region efficiency values 8.27% and 7.73% respectively were achieved, versus 6.50% for N719 without co-sensitization.

Also it was able to achieve the 7.0% and 7.7% efficiency of the cells due to the use of cis-squaraine dyes **26** and **27**, co-sensitized by benzothiadiazole dye **28**.^[83] The combination of these sensitizers provided panchromatic light absorption. Additionally, the authors paid attention to the selection of the optimum ratio of the dyes.

The co-sensitized DSSC with derivative of zinc phthalocyanine complex and triarylamine-bithiophene dye was created.^[84] As a result, it managed to increase the cell



Approaches to Improve DSSC Efficiency

efficiency to 6.61 %, which substantially exceeds the result for each of the dyes alone (2.38 % and 5.16 %, respectively). The authors of ^[85] modified the known indoline dye **29** (WS-2) and presented the synthesis of two new dyes **30** (WS-92) and **31** (WS-95), with which it was possible to achieve efficiency of DSSC 5.13 % and 7.69 %, respectively. For **31** together with a triarylamine-bithiophene dye efficiency was 9.18 %. Notable is the fact that the use of co-adsorbent only worsened the results, the authors explain it by the presence of octyl chains in **31**, which preventing aggregation, even in the absence of co-adsorbent.

Also, the use of co-adsorbent and co-sensitizers with porphyrin dyes **32** (XW9), **33** (XW10), **34** (XW11) was investigated.^[86] Among compounds **32** \rightarrow **33** \rightarrow **34** shortcircuit current increase and open-circuit voltage reduction were observed. By use of chenodeoxycholic acid for all dyes V_{oc} increase was achieved, but it is pointed out that because CDCA is not photoactive, its use results in a reduction of the I_{sC} , limiting the increase in overall efficiency. The authors proposed to use the triarylamine co-sensitizer **35** (C1), which compensates for the lack of porphyrin light absorption at wavelengths around 500 nm. Through the use of **35** managed to increase the current and voltage. The authors also examined the co-sensitizer **36** (WS-5), which also absorbs light in the portion of spectrum around 500 nm and provides a high V_{oC} . Through the use of **36** managed to achieve maximum results, including a high result in 11.5% efficiency for a sensitizers couple **34** and **36**.

The Choice of Electrolyte and Redox Couple

DSSC electrolyte is a redox medium in which the oxidized dye is reducing. Electrolyte components meet a number of requirements:

- 1. The redox couple should effectively regenerate the dye;
- The electrolyte must provide a fast diffusion of the charge carriers, have high conductivity, create an effective contact between the working and counter electrodes;
- The components of the electrolyte must have longterm chemical, thermal and thermo-chemical stability;
- 4. The electrolyte components should not be corrosive with other elements of the cell;
- 5. The electrolyte absorption spectrum components should not overlap with the dye absorption spectrum.

In the classical scheme of DSSC, proposed by Grätzel, a mixture of ethylene carbonate and acetonitrile 80:20 with addition of 0.5 M tetrapropylammonium iodide and 0.04 M iodine was used as an electrolyte. It is possible to





achieve significant results in terms of efficiency by using this electrolyte, but it may affect negatively on the electrode material and/or TiO_2 , thus providing poor stability for prolonged use.^[87]

In order to solve this problem, numerous other variants of electrolytes have been proposed by different scientific groups. Thus, the following redox pairs were used: $Br/Br_2^{[88]}$ SCN⁻/(SCN)₂,^[89] Co^{II}/Co^{III},^[90] but the results were inferior in comparison with I⁻/I, pair.

Another approach was the use of additives that exerted its effect by changing the redox potential, the semiconductor band shifts and influence on the dye surface organization.^[18] Most of these additives contain in their chemical structure an electron donor nitrogen heterocycle, for example 4-*tert*- butylpyridine. Influence of some such additives has been studied.^[91] Many additives of different structures have been studied by Kusama H., Arakawa H. *et al.*, particularly, pyridine quinoline and pyrazole derivatives studied.^[92–96] One of the most common agents as additive to the electrolyte became guanidine thiocyanate, which, due to the semiconductor band shift and slower recombination process it allowed to increase the open circuit voltage of the cell.^[97]

Among liquid electrolytes ionic liquids should be noted. They are salts in the liquid state which are thermally and chemically stable, have a high conductivity and relatively low vapor pressure at room temperature. Also, they can simultaneously serve as a solvent and carrier of iodine ions. Research of this type of electrolyte is represented, for example, in ^[98]. However, all liquid electrolytes have the disadvantage, especially important in the practical implementation of DSSC: the possibility of evaporation and leakage. Currently in the works devoted to the choice of electrolytes, there is a tendency to creation of solid and gel-like electrolytes.

A solid electrolyte based on lithium iodide and 3-hydroxypropionitrile which provide a spatial transfer of iodine was proposed.^[99] The authors faced with the problem of relatively low conductivity and poor photoanode surface contact with the electrolyte, which was partly solved by the addition of nano-sized particles of SiO₂.

A number of works are devoted to the electrolyte based on polymers. For example, lithium iodide complex with a mixture of polyethylene oxide and polydimethylsiloxane was proposed,^[100] but DSSC efficiency was low. Paper ^[101] described a number of poly(*N*-alkyl-4-vinylpyridine iodide) electrolytes, which permitted to significantly increase the efficiency of all-solid-state DSSC. The electrolyte based on 1-methyl-3-propylimidazole and iodine in polyethylene glycol dimethyl ether was described.[102] The authors investigated the effect of adding to such a system SiO, nanotubes, which form channels, improving the movement of ions. As a result, it was found that with increasing amount of nanotubes increased short-circuit current, improving the efficiency of DSSC with quasi-solid electrolyte. An electrolyte in the form of organic dicationic crystal based on benzothiazole was proposed.^[103] It was concluded that it is an effective matrix for the solid-state DSSC. In paper ^[104] pyrrolidinium ionic crystals, forming a three-dimensional ionic channels have been described, thus providing high efficiency and stability of the DSSC.

To date, DSSC with gel-type electrolyte are widespread. Authors ^[105] reported about the gel type electrolyte, which is obtained by in situ low temperature polymerization of 1,1'-(methylenedi-4,1-phenylene)bismaleimide polymerized in liquid electrolyte without an initiator. A thixotropic gel electrolyte based on xanthan gum was described.^[106] Addition of water to such an electrolyte provided open-circuit voltage increase, but at the same time led to short-circuit current reduction and reduced stability due to desorption of the dye. Paper ^[107] describes the preparation of an electrolyte with a controlled viscosity by applying polystyrene particles to a counter electrode. When valeronitrile added to liquid electrolyte, the particles were dissolved, turning the electrolyte in the gel-type (Figure 7). The effectiveness of these cells was comparable to the cells with a liquid electrolyte.

The effect of gelling agents on the parameters of the cell was investigated.^[108] The authors concluded that the

use of a gel-type electrolyte provides high stability during long-term tests, contributes to the increase in open-circuit voltage due to the shift of the TiO₂ conduction band edge and reduce recombination at the electrolyte/semiconductor interface, but it reduces the short-circuit current due to the slow ionic diffusion and limited charge transfer to the counter electrolyte.^[109] Egg albumin) was proposed as a gel electrolyte.^[109] Egg albumin was functionalized by ethylenediaminetetraacetic dianhydride whereby it was possible to increase the ability to form cross-linking and increase conductivity. The authors of ^[110] succeeded in increasing the open-circuit voltage due to the positive shift of the gel-type electrolyte redox potential. These results were obtained through the use of ZnAl layered double hydroxides additives.

Practical Use of DSSC

As it was noted in introduction, this review discloses scientific results for very small cells, which are studied in laboratory. Practical use of DSSCs requires to greatly enlarging of their surface area. But by surface area increasing the total efficiency decreases. In addition problems of longterm stability should be solved. So, there is still a lot of works in a field of DSSC up-scaling and optimization.

Notable progress was achieved by A. Hinsch *et al.*^[112-114] Authors developed a half-automated station for coloring and electrolyte filling made out of standard parts, which allows obtaining full-sized cells. Up to 7.1 % efficiency was reached for 10×10 cm modules; also 60×100 cm (6000 cm²) module was produced with 2.3 % efficiency. It is remarkable that authors pay attention to development of environment-friendly manufacturing process with recyclable module materials.

Conclusions

For two and a half decades, thanks to the efforts of many scientific groups, considerable progress in the field of dyesensitized solar cells has been achieved. The effectiveness of these devices has increased by 1 % to an impressive 13 %, which is subject to a number of other benefits may allow them to compete with classic silicon solar cells and ensure a significant role in the development of alternative energy. The attention of scientists to this area increases year by year. Despite the large number of studies already carried out, the



Figure 7. The scheme for obtaining a polystyrene gel-type electrolyte.^[107] Reprinted with permission from Lee K.S., Jun Y., Park J.H. *Nano Lett.* **2012**, *12*, 2233–2237. Copyright 2012, American Chemical Society.

optimization of DSSC is an urgent problem. In this review, we have demonstrated the most important in our opinion ways to improve the efficiency of photoelectric devices of this type, and also noted the latest developments in this field.

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