An improvement of the dye solar cell efficiency/ The electron shuttles role

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Motivation

The current annual energy consumption in the world is *ca.* 4.1 x 10**20 Joules. This figure tends to increase. Burning of hydrocarbons that produces the required amount of energy is too wasteful, and hydrocarbons as fuel will soon be exhausted. There are several ways to solve the problem of alternative energy for the Earth. The "Universal" one is to use solar energy. Indeed, due to estimations the Sun every hour gives *ca.* 4.3 x 10**20 Joules to Earth hour. The energy supplied by the Sun during the year is in 37668 times more than the Earth consumes. It is a truly inexhaustible resource. The challenge is to be able to use it

Photovoltaics: what is it ?

Photovoltaic cells or photovoltaic devices are those that are capable to generate electricity under direct or indirect exposure to light.

Operation of every photovoltaic device includes:

- An absorption of light followed by formation of “electron-hole” pairs or excitons.
- Charge separation giving carriers of different types (electrons move to one electrode, a hole - to another one).
- Extraction of carriers at the electrodes connected to an external electrical circuit.

There are several types of solar cells

1. Solar cells based on silicon

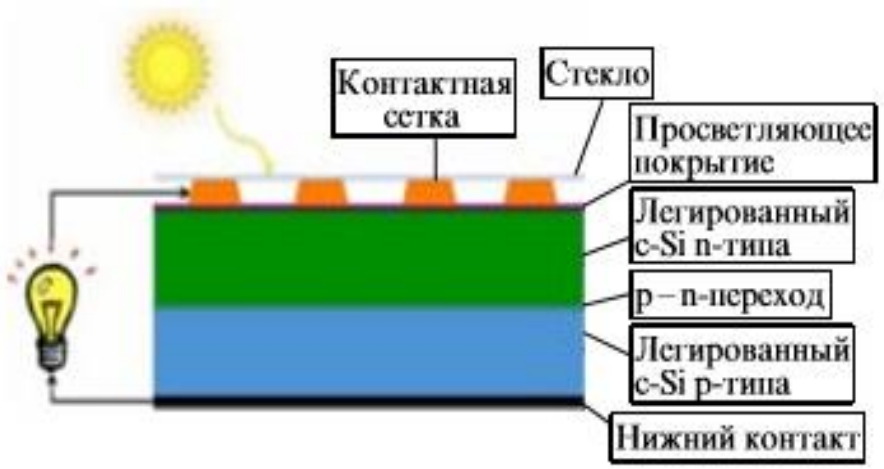
2. Solar cells based on dye sensitization

3. Organic Photovoltaics

4. The solar cell based on perovskite

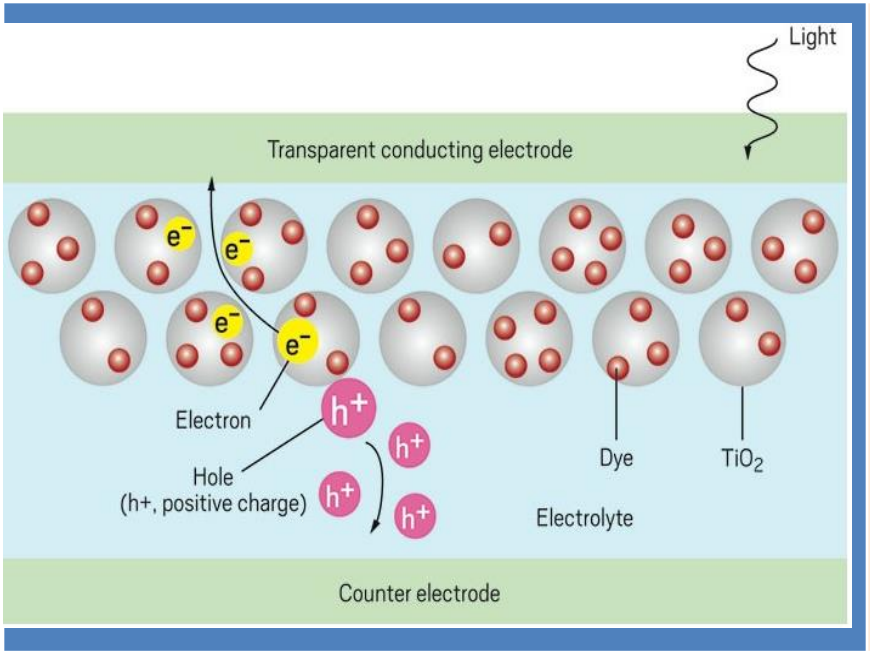
5. Photovoltaic based on quantum dots

Solar cells based on silicon



Миличко, В.А.; Шалин, А.С.; Мухин, И.С.; Ковров, А.Э.; Красилин, А.А.; Виноградов, А.В.; Белов, П.А.; Симовский, К.Р.; Солнечная фотовольтаика: современное состояние и тенденции развития, *Усп. Физ. Наук*, **2016,** *186 (8)*, 801-852

Solar cells based on dye sensitization



(From Mitch Jacoby, The future of low-cost solar cells, *Chemical & Engineering News*, 2016, *94(18)*, 30-35)

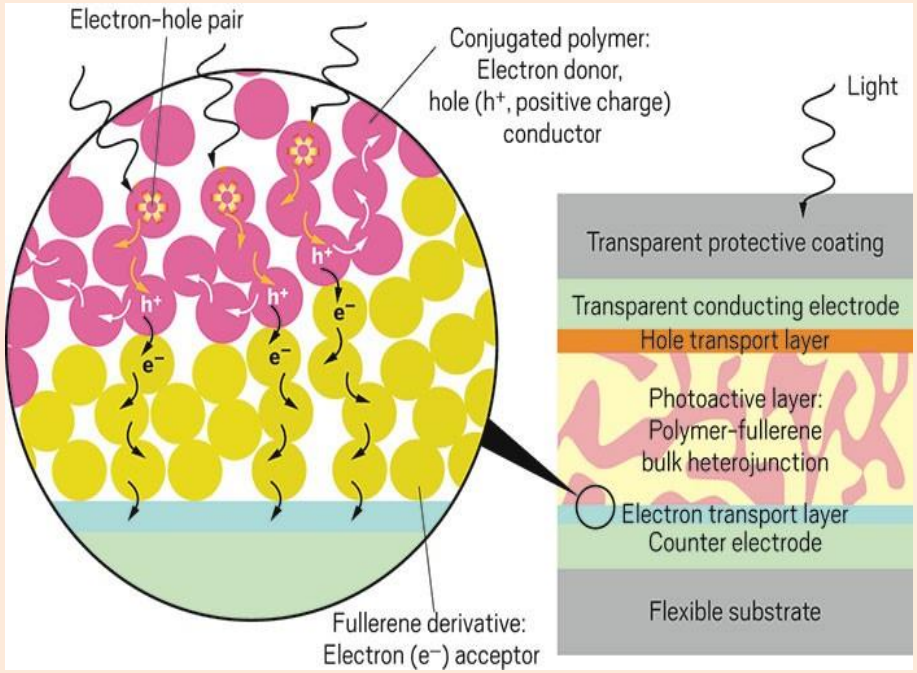
This slide is a diagram illustrating the principle of solar cells based on sensitization dyes. Light passes through the transparent electrode of the cell and is absorbed by the dye (red balls), which covers the particles of TiO2 (marked in gray).

As a result of the action of light, the charge separation with the formation of electron-hole pairs (e- / h +). The electron then travels through the TiO2 layer to one of the electrodes, while the hole moves to the other (blue) electrode. As a result, electric current is generated. The material for these cells are particles of TiO2, coated with a dye (ruthenium complexes are often used), absorbing light and well able to charge separation on the TiO2 surface. Typically, such particles are surrounded by a liquid-phase electrolyte

Solar cells based on dye sensitization

To improve the cells characteristics a liquid electrolyte instead of the semiconductor one was used $CsSnI_{2.95}F_{0.05}$ was used [Chung, I .; Lee, B .; He, J .; Chang, R. P. H .; Kanatzidis, M. G .; All-solid-state dye-sensitized solar cells with high efficiency, *Nature*, **2012**, *485*, 486-490; Ma, S .; Shang, M .; Yu, L .; Dong, L .; Device optimization of $CsSnI_{2.95}F_{0.05}$-based all-solid-state dye-sensitized solar cells with non-linear charge-carrier-density dependent photovoltaic behaviors, *J. Mater. Chem. A*, **2015**, *3*, 1222-1229]. Very encouraging results were obtained.

Organic Photovoltaics

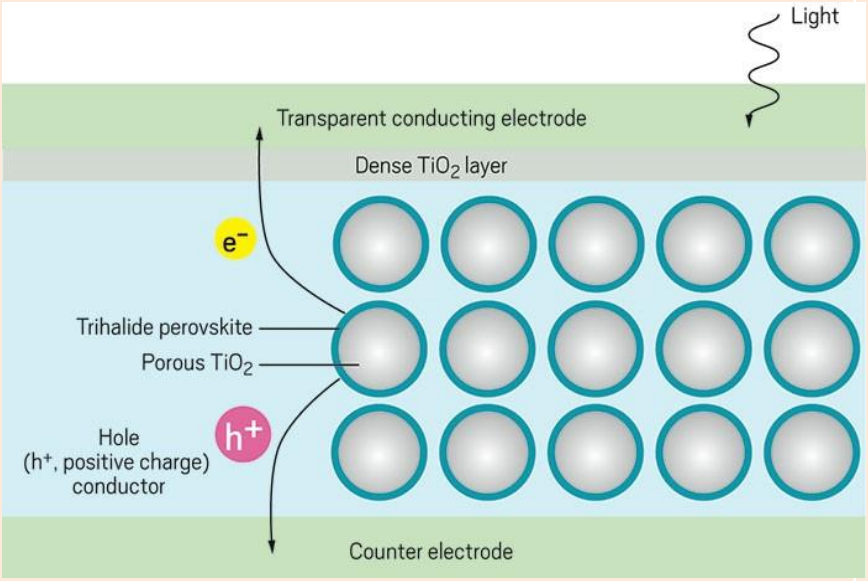


(From Mitch Jacoby, The future of low-cost solar cells, *Chemical & Engineering News*, 2016, *94(18)*, 30-35)

Light enters into an organic solar cell, passes through the transparent top layer and leads to charge separation in the organic photosensitive material. After that the formation of the "electron- hole“(e- / h +) pairs has place. Upon reaching the interface between the conductive polymer (pink) being an electron donor and a fullerene (yellow

layer) being an electron acceptor, a pair of splits into positive charges flowing down along nano-layer of conductive polymer to one of the electrodes and negative charges migrate through a layer of fullerene to another electrode. An electric current appears.

The solar cell based on perovskite

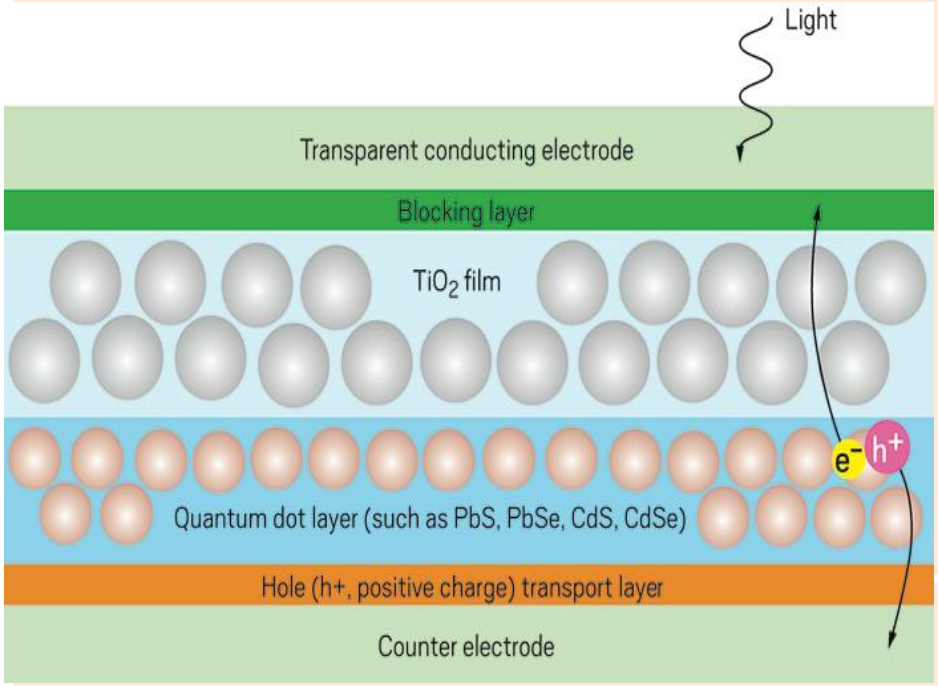


(From Mitch Jacoby, The future of low-cost solar cells, *Chemical & Engineering News*, 2016, *94(18)*, 30-35)

Light passes through the transparent electrode (labeled green) solar cell and falls on the layer of photosensitive perovskite material (blue) and stimulates excitation of photosensitive molecules that ultimately leads to charge separation and the formation of pairs of "hole-electron " (e- / h +). Further,

electrons and holes reach their electrodes, and an electric current.
These devices use perovskite compounds capable of absorbing light. The most studied example is the compound (CH3NH3) PbI3

Photovoltaic based on quantum dots



(From Mitch Jacoby, The future of low-cost solar cells, *Chemical & Engineering News*, 2016, *94(18)*, 30-35)

In solar cells based on quantum dots, nanocrystals used metal chalcogenides, have semiconducting properties, such as CdS, CdSe, PbS and PbSe, and other photosensitive materials. Under the influence of light materials such as charge separation occurs, i.e. pairing "electron-hole"(e- / h +).

The efficiency of solar cells

Material/ Method	Efficiency, %
Si, crystalline	25.6 +- 0.5
Si, multicrystalline	21.3 +- 0.4
Si, thin film submodule	21.2 +- 0.4
Si, thin film minimodule	10.5 +- 0.3
a-Si, amorphous	10.2 +- 0.3
a-Si/nc-Si/nc-Si (thin film) nc-Si=nano microcrystalline	13.6 +- 0.4
a-Si/nc-Si/nc-Si (thin film cell)	12.7 +- 0.4
Si, microcrystalline	11.8 +- 0.3
GaAs (thin film)	28.8 +- 0.9
GaAs (multicrystalline)	18.4 +- 0.5

Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E.D.; Solar cell efficiency tables (version 48), *Prog. Photovolt: Res. Appl.*, **2016**, *24*, 905–913

The efficiency of solar cells

Material/ Method	Efficiency, %
InP (crystalline)	22.1 +- 0.7
CIGS = CuInGaSe (cell)	21.0 +- 0.6
CIGS = CuInGaSe (minimodule)	18.7 +- 0.6
CdTe (cell)	21.0 +- 0.4
CZTSSe = CuZnSnSe (cell)	9.8 +- 0.2
CZTS = Cu_2ZnSnS_4 (cell)	7.6 +- 0.1
Perovskite (cell)	19.7 +- 0.6
5 junction cell	38.8 +- 1.2
InGaP/GaAs/InGaAs	37.9 +- 1.2
GaInP/GaInAs/Ge;Si (minimodule)	34.5 +- 2.0

Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E.D.; Solar cell efficiency tables (version 48), *Prog. Photovolt: Res. Appl.*, **2016**, *24*, 905–913

The efficiency of solar cells

Material/ Method	Efficiency, %
GaInP/GaAs (monolitic)	31.6 +- 1.5
GaInP/Si (mech. Stack)	29.8 +- 1.5
Dye sensitized (cell)	11.9 +- 0.4
Dye sensitized (minimodule)	10.7 +- 0.4
Dye sensitized (submodule)	8.8 +- 0.3
Organic (cell)	11.2 +- 0.3
Organic (minimodule)	9.7 +- 0.3

Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E.D.; Solar cell efficiency tables (version 48), *Prog. Photovolt: Res. Appl.*, **2016**, *24*, 905–913

Basic ways to increase the efficiency of solar cells

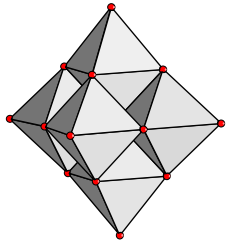
1. Increasing of the solar energy amount absorbed by the photoactive substance in the opto-electronic converter, including the use of photosensitizers (Grätzel) and of so-called solar concentrators;
2) The use of photochemically induced redox reactions allowing to convert light into chemical potential difference (Yachandra);
3) Increase the exciton transfer kinetics or photochemically induced electron transfer rate or transport of charge carriers;
4) Using coupled reactions with electron transfer, for example, by photocatalysis (Nocera)

5) Using the substances being able to shuttle electrons from a generation place to the metal electrode

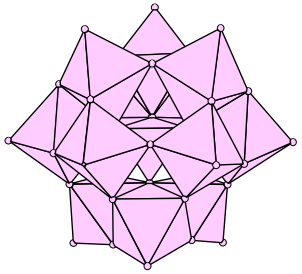
Polyoxometalate: typical structures

$$n\,[MO_4]^{2-} + p\,H^+ \longrightarrow POM + H_2O$$

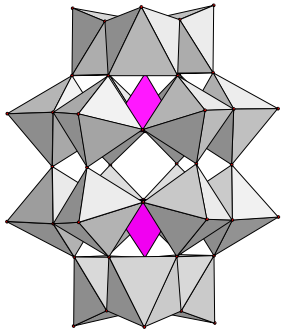
- ***Lindqvist anion: $[W_6O_{19}]^{2-}$***



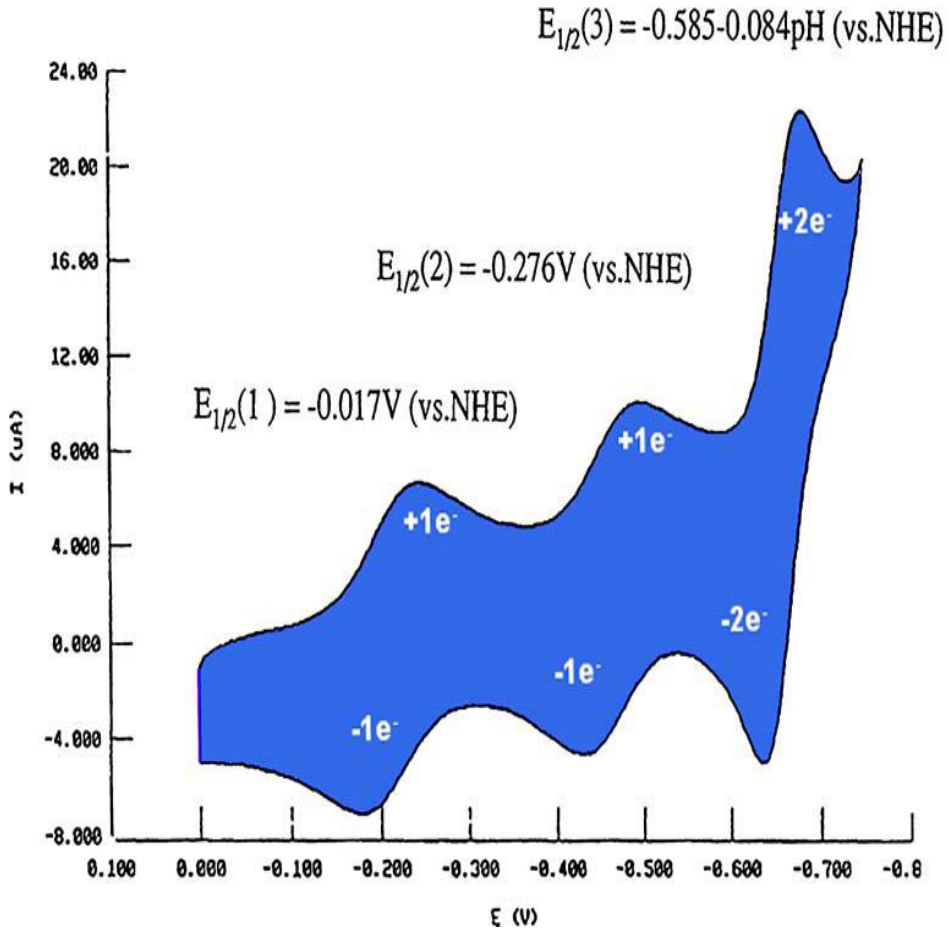
- ***Keggin anion: $[PW_{12}O_{40}]^{3-}$***



- ***Dawson anion: $[P_2W_{18}O_{62}]^{6-}$***



Cyclic voltammogram evidences about concecutive and reversible polyoxometalate $H4SiW_{12}O_{40}$ recovery



POM can be reversely recovered giving the mix-valent particles producing blue or brown color of an irradiated film *P. Gomez-Romero, K. Cuentas-Gallegos, M. Lira-Cantu, N. Casan-Pasror*, J. Mater. Sci., 2005, 40, 1423 – 1428

Photooxidation by POM

$$2H_3PW_{12}O_{40} + H_3CCH_2OH \xrightarrow{h\nu} 2H_4PW_{12}O_{40} + H_3CCHO \quad (1)$$

$$2H_4PW_{12}O_{40} + {}^1/_2O_2 \rightarrow 2H_3PW_{12}O_{40} + H_2O \quad (2)$$

$$[PW_{12}O_{40}]^{3-} \xrightarrow{h\nu} [PW_{12}O_{40}]^{5-} \quad (3)$$

$$[PW_{12}O_{40}]^{5-} \xrightarrow{O_2} [PW_{12}O_{40}]^{5-} + O_2^{2-} \quad (4)$$

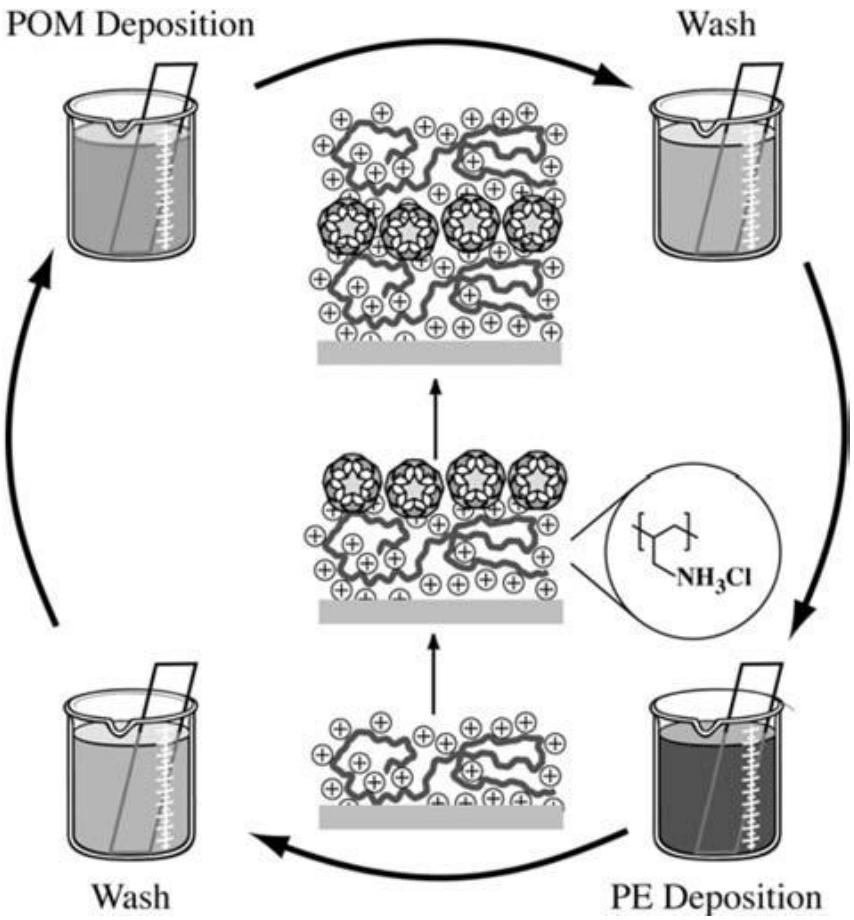
Toshihiro Yamase, *Chem. Rev.* 1998, *98,* 307-325

Conductance of POM

POM	Conductance (S/cm)
$H_3PW_{12}O_{40}.14H_2O$	3.3×10^{-4}
$H_3PW_{12}O_{40}.29H_2O$	8×10^{-2}
$Rb_3PW_{12}O_{40}.6H_2O$	1.7×10^{-2}
$Cs_3PW_{12}O_{40}.8H_2O$	2.5×10^{-2}
$Na_3PW_{12}O_{40}.16H_2O$	6.6×10^{-5}
$Li_3PW_{12}O_{40}.27H_2O$	1.25×10^{-2}

Ubavka b. Mioc, Marija R. Todorovic, Snezana M. Uskokovic-Markovic, Zoran P. Nedic and Nada S Bosnjakovic, *J. Serb. Chem. Soc.* 65(5-6), **2000**, 399

Layer-by-layer technology to form POM films



S. Liu, D. Volkmer, D. G. Kurth, Functional Polyoxometalate Thin Films via Electrostatic Layer-by-Layer Self-Assembly, *J. Cluster Science*, 2003, V. 14, No. 3, P.405-419.

The photovoltaic application of POM

Metallic cathodes made of a metal having a high work function. Due to high optical interference & reflectivity such metals as aluminum and the like should retard photogeneration of charges as a result of opto-electric field decreasing effect in the proximity of the electrode. Polyoxometalates could be deposited as thin layers between the active layer and the aluminum cathode to obtain the air exposure stability of hybrid inorganic polymer films for photovoltaic devices with improved characteristics.

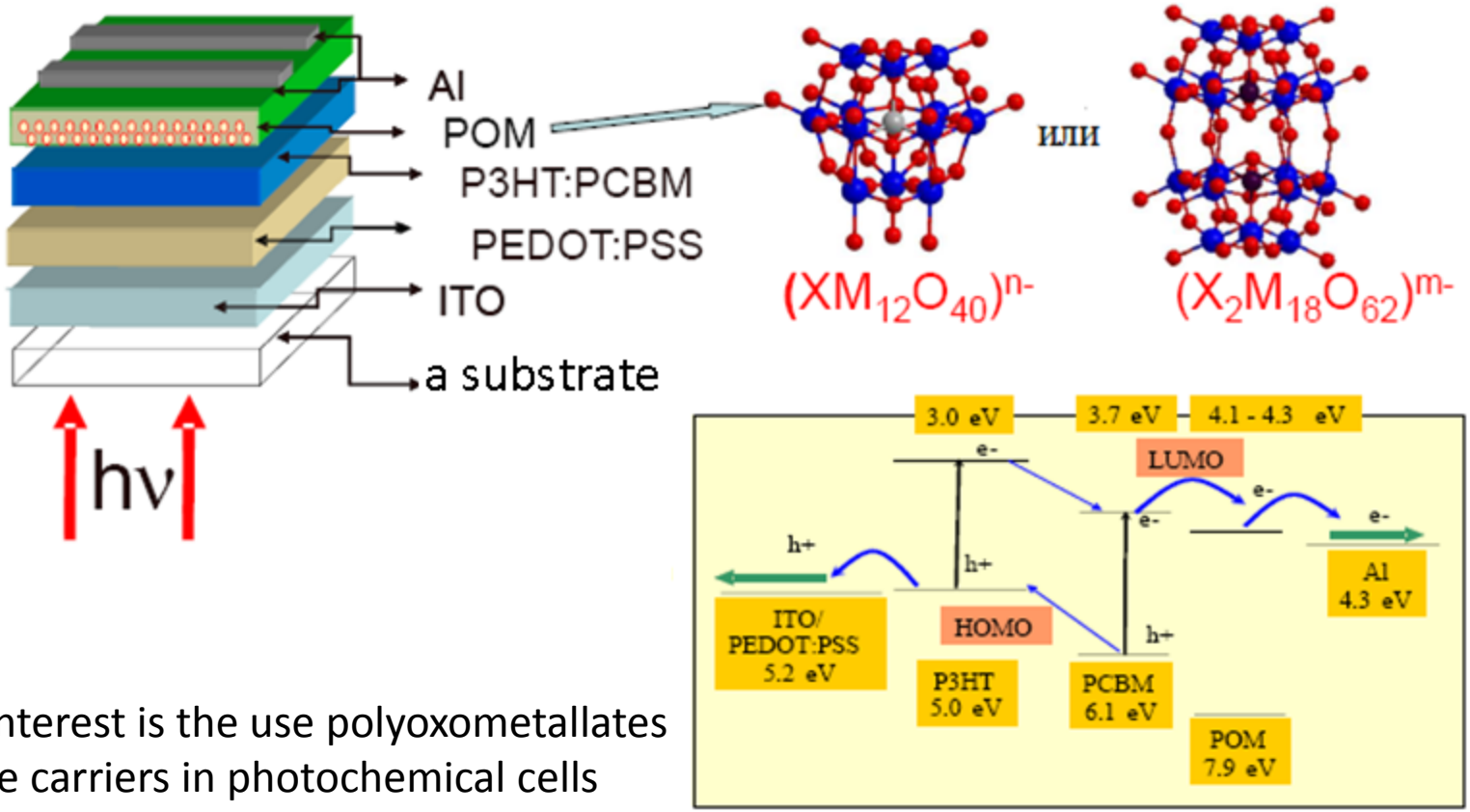
L. C. Palilis, M. Vasilopoulou, K. Kotsovos, A. Botsialas, E. Ntantoumis, A. M. Douvas, P. Argitis, // ***S2.3-O-Pallilis.pdf***

The photovoltaic application of POM

Introduction of a liquid layer containing dissolved POM between the active layer and aluminum cathode results in the photocurrent increase and efficiency of PV also increases in 1.5 times. In the case of PV improved absorption capacity of the photoactive layer and the spatial redistribution of the light in the thickness of the layer due to the greater size of the photogenerated current. Moreover, it is believed that the ability to block excitons POM, due to their large band gap can reduce the loss of excitons at the boundary between Al / POM and increases the magnitude of the photocurrent in the PV

L. C. Palilis, M. Vasilopoulou, K. Kotsovos, A. Botsialas, E. Ntantoumis, A. M. Douvas, P. Argitis, // S2.3-O-Pallilis.pdf_2

Polyoxometallates as the electron shuttles from their generation place to one of the electrode



Also of interest is the use polyoxometallates as charge carriers in photochemical cells based on TiO2 [R.R. Ozer, J.L. Ferry, Environ. Sci. Technol., 2001, 35, 3242] in acid electrolytes and fuel Enrgy, 1997, 22, 8009].

The photovoltaic application of POM

Using polyoxometallates allows

1) to apply solution technology;

2) to improve the electronic conductivity and transparency,

3) to adjust the levels of the highest occupied molecular orbital and the lowest unoccupied molecular orbitals to improve the extraction of electrons and blocking holes (i.e. reduce the negative contribution of the charge recombination of electrons near electrodes).

The photovoltaic application of POM

Sung et al. [Sang, X.J .; Li, J.S .; Zhang, L.C .; Zhu, Z.M .; Chen, W.L .; Li, Y.G .; Su, Z.M .; Wang, E.B .; Two carboxyethyltin functionalized POM for assembly on carbon nanotubes as efficient counter electrode materials in dye-sensitized solar cells, Chem. Commun. (Camb.), 2014, 50 (93), 14678-14681] have reported the synthesis of new hybrid POM modified carboxyethyltin fragments. The authors used these compounds as additives that increase the electrocatalytic activity of carbon nanotubes applied to restore triiodide. The tubes were used as substitutes for platinum counter electrodes in solar cells. The efficacy of the modified tube was 6.32%, whereas the efficiency in the use of platinum electrodes was equal to 6.29%.

The photovoltaic application of POM

Guo et al. [Guo, X.-W .; Li, J.-S .; Sang, X.-J .; Chen, W.-L .; Su, Z.-M .; Wang, E.-B .; Three Keggin-Type Transition Metal-Substituted Polyoxometalates as Pure Inorganic Photosensitizers for p-Type Dye-Sensitized Solar Cells, *Chemistry - A European Journal*, **2016**, *22 (10)*, 3234-3238] have evaluated the potential use of POM substituted by transition elements such as $TBA_8Na_2[SiW_9O_{37}\{Co(H_2O)_3\}] \cdot 11H_2O$, $TBA_4[(SiO_4)W_{10}Mn^{III}{}_2O_{36}H_6] \cdot 1.5CH_3CN \cdot 2H_2O$ and $TBA_{3.5}H_{5.5}[(SiO_4)W_{10}Mn^{III/IV}{}_2O_{36}] \cdot 10H_2O \cdot 0.5CH_3CN$ where TBA = $(n\text{-}C_4H_9)$ 4N + as photosensitive agents working in solar cells belonging to the class of cells sensitized with dyes. Their effectiveness in 2.23, 1.71 and 1.59 times higher than commonly used dye coumarin 343.

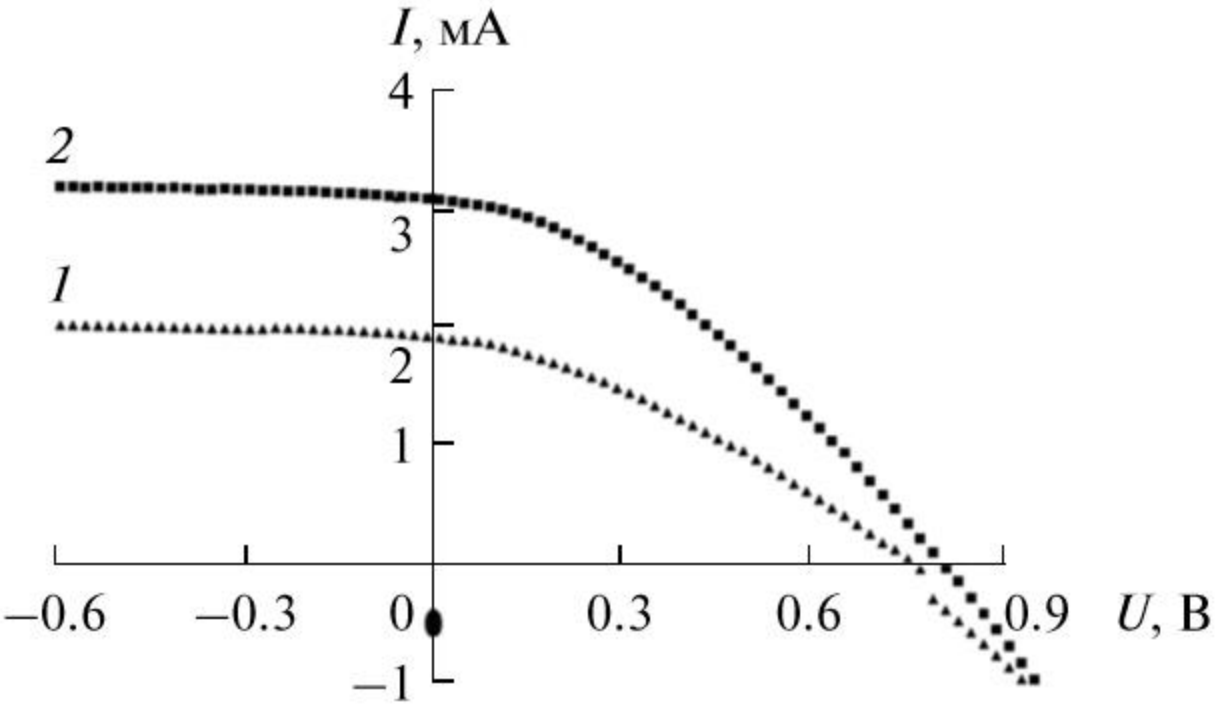
The photovoltaic application of POM

Guo et al. [Guo, X.-W .; Li, J.-S .; Sang, X.-J .; Chen, W.-L .; Su, Z.-M .; Wang, E.-B .; Three Keggin-Type Transition Metal-Substituted Polyoxometalates as Pure Inorganic At the Almeida [Almeida, L. C. P .; Gonçalves, A, D .; Benedetti, J. E .; Miranda, P. C. M. L .; Passoni, L. C .; Nogueira, A. F .; Preparation of conducting polyanilines doped with Keggin-type POM and their application as counter electrode in dye-sensitized solar cells, *J. Mat. Sci.,* **2010**, *45 (18)*, 5054-5060] have described the conductive polymers polyaniline doped by the Keggin type POM. Conductive polymers have a conductivity of up to 0.1 S cm-1. They have been used as a new type of efficient counter electrodes in solar cells sensitized with dyes.

POM application: our work

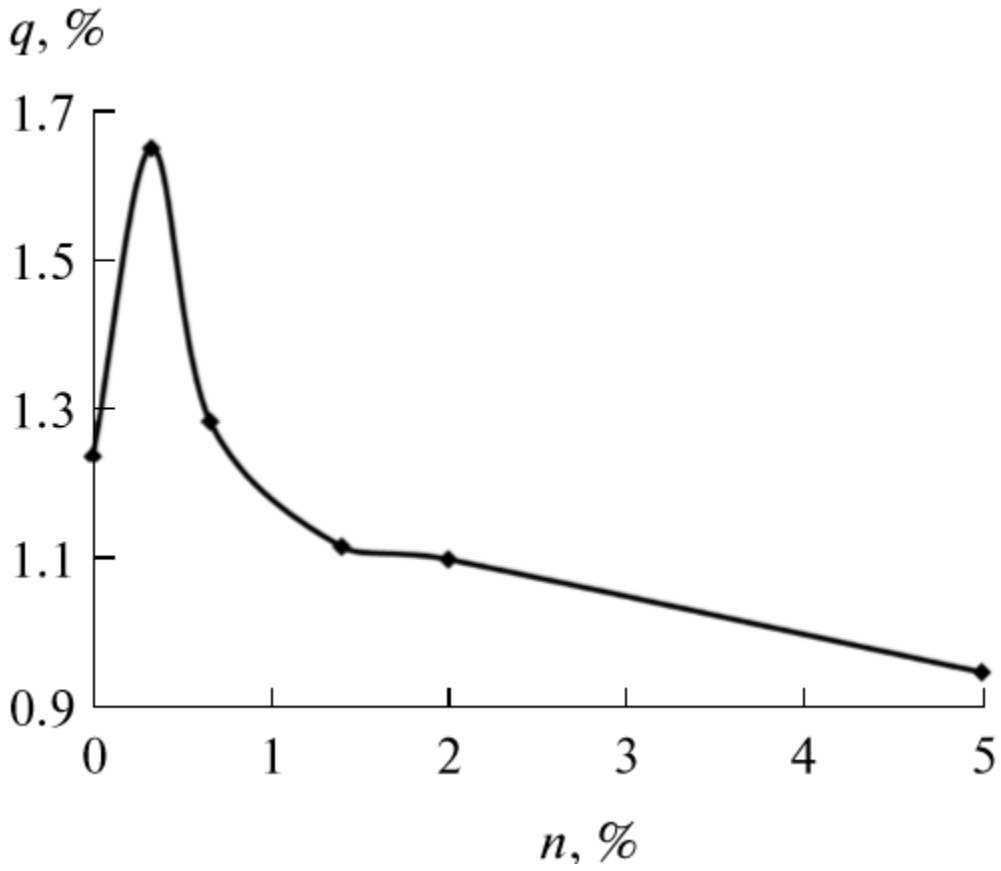
Let us consider in more details our work on the effect of the introduction of POM on efficiency of photovoltaic cells [Logunov, A. A .; Machines, A. I .; Zelentsov, S. V .; Kudryashov, M.A .; Nezhdanov, A. B .; Ryabov, A. C .; Chidichimo, G .; De Filpo, G .; Effect of polyoxoanions of phosphotungstic acid on photoconversion efficiency of dye-sensitized solar cells based on titanium dioxide, *High Energy Chemistry*, **2016**, *50 (3)*, 195-197]. We have developed a method of forming of composite photoanodes of TiO_2 and POM - phosphotungstic acid, $H_3[PW_{12}O_{40}]$. Introduction of POM in the porous layer increases the efficiency of TiO_2 dye-sensitized solar cells and affects characteristics such as the open circuit voltage and short circuit current.

POM application: our work



The current-voltage characteristics of solar cells on a porous electrode from 1 - TiO2, 2 - TiO2 + 0.33% phosphotungstic acid. Thus adding of only 0.33% of POM to TiO2 leads to increasing of current efficiency by 1.5 times.

POM application: our work



The dependence of the efficiency of solar cells on the content of polyoxometalates in porous titania electrode, where q - efficiency, n - weight content H3 [PW12O40].

Mechanism of the POM involvement

$$TiO_2 + [RuL_4]^* \xrightarrow{h\nu} e^-_{CB} + [RuL_4]^+, \quad (1)$$

$$e^-_{CB} + POM \rightarrow POM^-, \quad (2)$$

$$POM^- \xrightarrow{h\nu} POM^{-*}, \quad (3)$$

$$POM^{-*} + TiO_2 \rightarrow POM + e^-_{CB}. \quad (4)$$

In addition, the discharge polyoxometallates anion can occur on collecting electrons of the metal electrode.

POM^- + AL (electrode) → POM + AL (electrode) (5)

Mechanism of the POM involvement

The dye in the excited state injects electrons into the conduction band of TiO2. Then, the electrons moves to the collecting electrode. This process faces two competing reactions, namely, capture of an electron from the conduction band by the dye oxidized form to form the dye in the ground state, and there has place an interaction between the electron and the electrolyte. POM accepts an electron from the conduction band of TiO2, forming a reduced form, the latter under the action of light becomes excited and deactivates by an injection of electrons back into the conduction band of TiO2. Thus, the presence of POM increases “efficient” lifetime of charge carriers that leads to an increase of the cell efficiency. A further increase in concentration leads to a decrease in cell efficiency due to a kind of POM “dilution”, reducing the TiO2 content in the porous electrode, and accordingly, and the adsorbed dye. As a result, less and less absorbed photon generated charge carriers. Second, at high concentrations POM are possible concentration quenching and other decontamination processes.

Thus, we have shown that solar cells that are based on the modified photoanode demonstrate the extreme dependence between the energy

Outlook

Unfortunately, I had not enough time to talt about very important point: theoretical description of the photochemical charge separation and following dissipation of the corresponding excited states. Recently developed quantum chemistry methods such as Real Time TD DFT anf the like methods gives an unique chamce to “see” the chronics of the molecular movements in the time period from the light irradiation and the charge separation (about 300 fs. It seems me important to outline the possibility. As far as I know there are only a few papers devoted the theoretical investigation in the area but it seems me such investigations waite their time/

Great thanks to all who have listen to my talking and the seminar organizers to gain us a possibility to have fruitful discussion.