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APPLICATIONS OF SEMICONDUCTOR NANOPARTICLES IN POWER INDUSTRY

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Summary. Semiconductor nanoparticles have been applied mainly to construct a new type of solar cells. Solar cells, which work on the basis of a solid-state junction (photovoltaic cells), are often replaced by photoelectrochemical cells. The photovoltaic cells are made of doping silicon and their maximal sensitivity, corresponding to the solar radiation placed on the wavelength reaches 650 nm - whereas the photoelectrochemical cells are made of dye-sensitized complex. Both complex compounds, i.e. dye and semiconductor, are matched to each other to absorb light from the visible range. The development of the photoelectrochemical cells is promoted by increasing public awareness that the Earth's oil reserves could run out during this century. Public concern has been also heightened by the disastrous environmental pollution arising from all-to-frequent oil spills and the frightening climatic consequences of the greenhouse effect caused by fossil fuel combustion.

Key words: nanoparticles, photoelectrochemical cells, oil reserves, greenhouse effect

1. INTRODUCTION

Increasing demand for energy is the main reason for developing alternative sources of electricity such as water, wind or Sun, which are friendly to the environment. Other reasons are increasing public awareness of running out of fossil fuels in this century, growing environmental pollution and connected with it – the green-house effect. Fortunately, the most efficient natural source of energy is the Sun which supplies $3 \cdot 10^{24}$ joules a year of energy to the Earth's surface. It is about 10 000 times more than the global population currently consumes. In other words, covering 0.1% of the Earth's surface with solar cells with an efficiency of 10% would satisfied our present needs [5]. Unfortunately, the silicon solar cells are characterized by small solar energy-to-electricity conversion efficiency. Nowadays, there are used mainly semiconductor nanoparticles, nanocrystalline etc. to construct a new type of energy source. Physical and chemical properties of the nanocompounds provide two ways of using them for industrial purposes like photocatalysis and conversion of solar energy into electricity in solar cells [13].

Solar radiation (sunlight) is the flux of electromagnetic waves and elementary particles given off by the Sun. The sunlight intensity on the upper part of the Earth's atmosphere is described by solar constant. The solar constant is the amount of incoming solar electromagnetic radiation per unit area that would be incident on a plane perpendicular to the rays, at a distance of one astronomical unit (the mean distance from the Sun to the Earth). Value of the solar constant is 1366.1 W/m^2. It fluctuates by about ±3.4% during a year due to the Earth's varying distance from the Sun. Spectral resolution of the sunlight is similar to the perfect radiator of temperature about 5800 K. Energy maximum is placed at the wavelength of 500 nm. Half of the solar energy corresponds to the visible light, whereas the other part is connected with ultraviolet and near-infrared. The solar radiation is weakened by the atmosphere due to absorption, reflection and scattering. About 30% of the sunlight is reflected by the atmosphere, 20% of it is absorbed, while only 50% reach the Earth's surface.

Photocatalysis is one of the semiconductor applications. It is defined as the acceleration of chemical reaction by the sunlight [11, 18]. This process is used to water splitting, organic molecules mineralization and carbon dioxide binding [16]. Titanium dioxide (TiO_2) nanoparticles are the most popular and promising photocatalyst. There are a few advantages of TiO_2. One of them is stability in various solvents. Furthermore, TiO_2 is not destroyed under the influence of light, is common, and can induce different types of chemical reaction [16, 39]. The semiconductor is characterized by a high photocatalytic activity if it is used in the form of nanoparticles because of a large surface area. For this reason, a large amount of molecules can adsorb on the nanoparticle surface. Furthermore, nanocrystallites should be heavily doped to decrease a recombination rate of the electron – hole (e^- - h^+) pairs [16]. Photcatalytic process starts when light of an adequate energy falls on the photocatalyst's surface. There is formed an electron – hole pair on the TiO_2 surface. The electrons react with an oxygen from the air, forming active oxygen, while hydroxide radicals are formed in reaction of the holes with steam or water. The radicals are strong enough to oxidize various types of organic pollutants e.g. exhaust fumes.

Titanium dioxide (TiO_2) is used in photocatalysis as well as in solar cells the most often because of its availability and low price. It is included to the wide band gap semiconductors with $E_g = 3.2$ eV. Hence, formation of the e^- - h^+ pair is caused only by photons of energy corresponding to the ultraviolet wavelengths. The charge carriers move to the semiconductor surface where react with adsorbed molecules or recombine. The charge carriers recombination is undesirable process [39].

The sunlight is also used in the solar cells to converse solar energy to electricity. The aim of this article is to present construction scheme and principle of operation of the nanoparticles solar cells.

2. SOLAR CELLS

Solar cells converse solar energy into electricity. Nowadays, conventional solar cells work on the basis of solid-state junction (p-n junction) using photovoltaic phenomenon. They were invented in the 1950s and first commercialized in the 1960s for use in the space program. Since then, there have been observed rapid development in the efficiency and reliability of these cells, along with substantial decrease in cost [6]. However, a solar energy-to-electricity conversion efficiency of these cells equals 10% and cost of their production is still too high to use it commonly as an electricity source. Hence, there is seen a continuous development of new substances which are characterized by a high conversion efficiency as well as a low cost of production. It can be included conducting polymers and surface complexes to such compounds. The surface complex consists of a wide band gap semiconductor (TiO_2, SnO_2, ZnO) in the form of nanoparticles and molecules. The molecules are adsorbed chemically on the nanoparticle surface and absorb light from the visible region or near-infrared [5, 26]. Adsorption of the molecules on the semiconductor surface with simultaneous decrease in the photon energy, which is adsorbed by the semiconductor nanoparticle, is well known as photosensitization. Catechol is an example of the photosensitizer which shifts a TiO_2 absorption maximum from 370 to 420 nm.

2.1. PHOTOVOLTAIC PHENOMENON

Both conventional and photoelectrochemical cells work on the basis of photovoltaic phenomenon. It was discovered by Edmund Becquerel in 1839. Becquerel illuminating solutions containing a metal halide salt observed a current between two platinum electrodes immersed in the electrolyte. This phenomenon has been applied mainly in the photography since silver halides have been used as a photographic emulsion. Initially, films were sensitive only to light of wavelength smaller than 460 nm in the XIX century. This is now recognized as being due to the semiconductor nature of the silver halides grains (AgF, AgCl, AgI, AgBr). Their band gap ranges from 2.7 to 3.2 eV, so they absorb only ultraviolet. In 1883 Vogel discovered that emulsion photosensitivity could be extended to the longer wavelengths by adding an adequate dye. A few years later Vogel's discovery was applied in photoelectrochemical cells by Moser. He used erythrosine as a dye on silver halide electrodes [5].

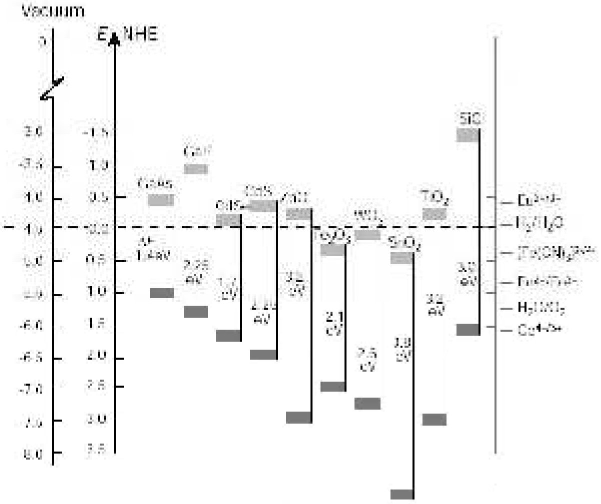

Fig. 1. Band gap position of several semiconductors forming junction with electrolyte at pH 1 using the vacuum level as a reference. The normal hydrogen electrode was used as a reference for standard potential of several redox couples [5]

Nowadays, there are carried out researches on looking for new photosensitizers which absorb light from the visible region. To this group are included: dihydroxyanthraquinones [12, 17, 25, 31], photosynthetic [21] and fluorescence dyes [33, 35], metal complexes of ruthenium [8, 19] and iron [15, 37]. Furthermore, titanium dioxide (TiO_2), zirconium oxide (ZnO), tin dioxide (SnO_2), niobium oxide (Nb_2O_5) and cadmium selenide (CdSe) are the semiconductors with an adequate band gap. Semiconductors and dyes are matched to each other very carefully. It is connected with the energy of semiconductor conduction band and dye excited state. Both states must have similar energy to allow fast transition of electron from the excited state to the conduction band. Electrolyte, characterized by a redox potential, also has to lie in the semiconductor band gap (see Fig.1). It is used the normal hydrogen electrode as a reference to measure the redox potential. The main reason of such procedure is to allow electrons free flow between parts of the system: semiconductor – dye – electrolyte – external circuit.

There are included regenerative, photosynthetic, dye-sensitized and ETA (extremely thin absorber) cells to the photoelectrochemical cell group.

2.2. REGENERATIVE AND PHOTOSYNTHETIC CELLS

Regenerative cells converse the solar energy into electric power without net chemical changes. Operation principle of this kind of solar cells is shown in figure 2. The electron – hole pairs are generated by incident light of energy exceeding that of the band gap. The pairs are separated by the electric filed present in the semiconductor – electrolyte interface. The negative charge carriers (electrons) move through the bulk of the semiconductor to the current collector and the external circuit. The positive holes are driven to the interface where they are scavenged by the reducing agent (Red) in the electrolyte. They are also oxidized. The oxidized form (Ox) is reduced back to the Red by the electrons that re-enter the cell from the external circuit [5].

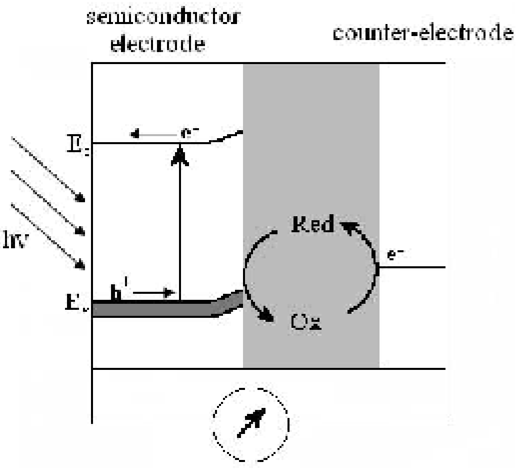

Fig. 2. Principle of operation of regenerative-type solar cell

Photosynthetic cells operate on a similar principle except that there are two redox systems (see Fig.3). One of them reacts with the holes at the semiconductor surface, while the second reacts with the electrons entering to the counter-electrode. This kind of electrochemical cells is used to produce a chemical fuel, hydrogen, through the cleavage of water by sunlight. The water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode [5].

There is used the titanium dioxide (TiO_2) as a semiconductor. However, it absorbs only ultraviolet due to energy of its band gap (E_g = 3.2 eV). Thus these cells exhibit a low value of IPCE (an induced-photon-to current conversion efficiency) [5].

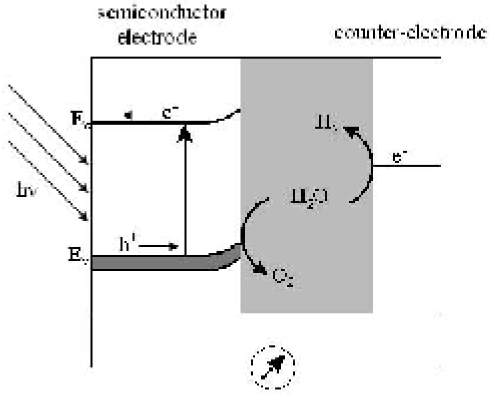

Fig. 3. Principle of operation of photosynthetic electrochemical cell

2.3. DYE-SENSITIZED SOLAR CELLS

To increase conversion efficiency of the electrochemical cells there have been used dye-semiconductor complexes. The semiconductor has a wide band gap, so absorbs light from the ultraviolet region, whereas dye, adsorbed at the semiconductor surface, absorbs visible light. Semiconductors with band gaps narrow enough for efficient absorption of visible light are unstable against photocorrosion and they are not utilized to construct these cells [5]. Dye-sensitized cells have one advantage in comparison with conventional solar cells. They separate light absorption from the transfer of charge carriers [7].

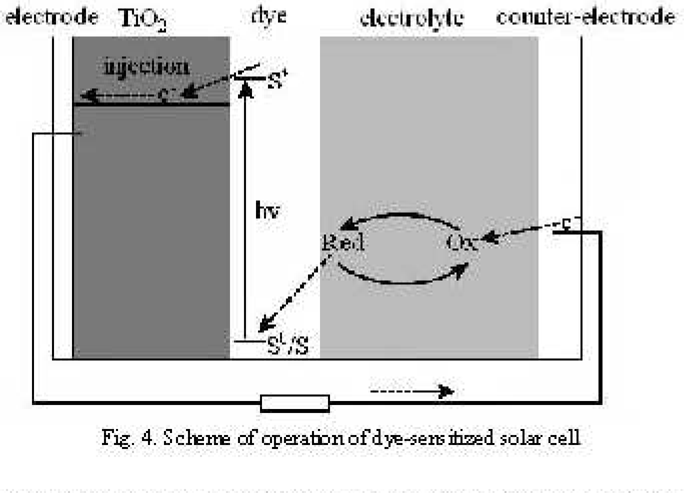

Fig. 4. Scheme of operation of dye-sensitized solar cell

Figure 4 depicts principle of operation of the dye-sensitized solar cell. Semiconductor electrode is sensitized by the ruthenium complex $RuL_2(SCN)_2$ (L is 2,2'-bipyridyl-4-4'-dicarboxylate). The ruthenium complex is considered to be the best photosensitizer because of strong absorption band in the visible region, long-life excited state and photochemical stability [27]. The complex is adsorbed on the mesoporous surface of TiO_2. Electrolyte contains I^-/I^-_3 redox system. The ruthenium complex plays the same role as a chlorophyll in a green leaf. It absorbs incident light and induces oriented transfer of electrons. The TiO_2 layer in the cell acts as a lipid membrane in the leaf. The dye adsorbs on the layer which also transfers electrons to the external circuit. This layer is mesoporous and a large number of dye molecules can be adsorbed on it. Hence the IPCE of this kind of solar cells increases to 80% in comparison with a cell of a flat layer of TiO_2. Both types of the cells were sensitized by the ruthenium complex [5].

Operation of dye-sensitized electrochemical cell is started by the photoexcitation of the dye (ruthenium complex) adsorbed on the semiconductor (TiO_2) photoanode. The electron is transferred from the metal (Ru) to the ligand. In the next step electron is injected to the conduction band from a molecular orbital of the dye. Photoinduced electrons move through the semiconductor layer to the conducting glass. Part of them are driven to the cathode because the dye have to be regenerated. The negative charge carriers are transferred through the redox system to the dye [27].

The dye-sensitized solar cells can be classified into two types, Type I and Type II, depending on the electron-injection pathway from the dye to the conduction band of TiO_2. Principle of operation of these solar cell types is shown in figure 5 [32]. The first pathway is photoexcitation of the local band of the adsorbed dye followed by electron injection from the excited dye to the conduction band. IPCE of these cells is about 11%. These dyes are classified as Type-I dyes. To this group belong dyes with a carboxylic unit such as Ru (II) complexes [5, 20, 38], coumarin derivatives [9, 10, 34] and metal-porphyrin complexes [1, 14]. Another pathway is direct electron injection from the ground state of the dye to the TiO_2 conduction band. The IPCE of the Type II cells does not exceed 0.7%. Type-II dyes include enediols (aromatic compounds having two hydroxyl groups) and compounds with nitrile groups. Catechol [22, 24, 28], dopamine [2, 24], fluoron [3] and ascorbic acid [23, 36] are examples of such dyes.

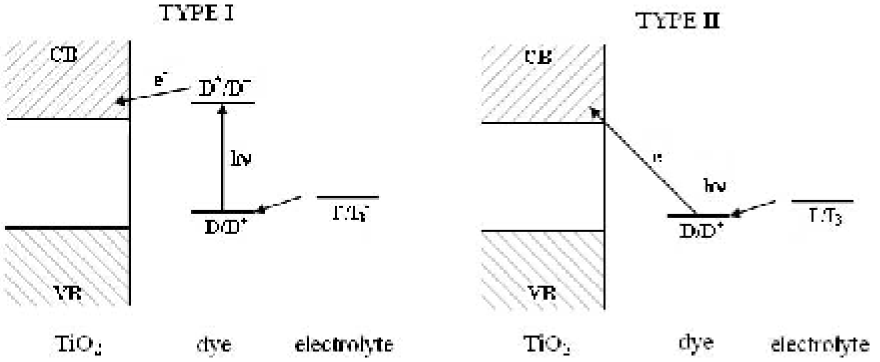

Fig. 5. Schemes of two electron injection pathways from adsorbed dye to TiO_2 in dye-sensitized solar cells

Dye-sensitized solar cells are characterized by the ultrafast electron injection from the dye to the conduction band occurring in time range of pico- and femtoseconds. Whereas the back-electron transfer from the semiconductor particle to the oxidized sensitizer occurred with a rate that was several orders of magnitude slower than the forward injection (microseconds) [4, 8, 12]. This process is probably connected with a small overlapping of dye molecular orbitals with 3d orbitals of titanium which form the conduction band [7]. There has been observed the fastest electron injection process of 3 femtoseconds in a bi-isonicotinic acid, so far [30].

2.4. ETA CELLS

Extremely thin absorber (ETA) solar cells are conceptually close to the dye-sensitized cells. The molecular dye is replaced by an extremely thin (2÷3 nm) layer of a narrow band gap semiconductor like $CuInS_2$. A compound, which acts as a hole conductor, is placed on top of the absorber, producing a PIN junction (p-type semiconductor – insulator – n-type semiconductor). This junction enhances light harvesting due to the surface enlargement and multiple scattering, which is considered as a big advantage. Furthermore, higher levels of defects and impurities are tolerated in these cells because photo-induced charge separation occurs on a length of a few nanometers. On the other hand, production of PIN-type solar cells of such high contact area is difficult and their conversion efficiency remains below 5% [5].

3. ADVANTAGES AND DISADVANTAGES OF PHOTOELECTROCHEMICAL CELLS.

Photoelectrochemical cells are now under intensive investigation. They have a lot of advantages such as low cost of production and simple and fast production technology comparing to conventional solar cells. Furthermore, some of semiconductors and dyes are easily available and IPCE conversion increase to 80% [5]. On the other hand, instability under incident photons is considered as undesirable process. There is a small amount of dyes and semiconductors compatible enough to absorb light from the ultraviolet and visible region and effectively converse photons into electricity. But dye-sensitized solar cells will be competitive with conventional silicon solar cells.

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ZASTOSOWANIE NANOCZĄSTEK PÓŁPRZEWODNIKOWYCH W ENERGETYCE

Streszczenie. Nanocząstki półprzewodnikowe stosowane są w przemyśle energetycznym głównie do budowy nowej generacji baterii słonecznych. Baterie słoneczne, działające w oparciu o złącze p-n, są coraz częściej wypierane przez ogniwa fotoelektrochemiczne. Tradycyjne ogniwa fotowoltaiczne wykonywane są zazwyczaj z domieszkowanego krzemu i charakteryzują się maksymalną czułością odpowiadającą promieniowaniu słonecznemu o długości fali około 650 nm. Natomiast w przypadku ogniw fotoelektrochemicznych tak można dobrać kompleks półprzewodnik – barwnik, aby światło było absorbowane z prawie całego zakresu widzialnego. Rozwój badań nad nowymi materiałami do budowy baterii słonecznych związany jest ze wzrastającą świadomością ludzi o tym, że zapasy paliw kopalnych wyczerpią się w niedługim czasie. Poszukiwania te związane są również ze stale rosnącym zanieczyszczeniem powietrza i związanym z nim efektem cieplarnianym, powstającym w czasie spalania paliw kopalnych.

Słowa kluczowe: nanocząstki, ogniwa fotoelektrochemiczne, zapasy paliw kopalnych, efekt cieplarniany