Photoelectrochemical Cells for a Sustainable Energy

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With the increasing demand of the energy, researches have focused more on sustainable energy production. Photoelectrochemical cells has been one of the solution for the energy crisis. Most of the devices contain solid state junctions which contain Silicon. With the emerging of new technologies, Silicon can be replaced by conducting polymer cells and nanocrystalline materials. Advantages of these materials are massive. In this paper some of the chemistry behind these solid state junctions are discussed in brief.

With the discovery of photoelectric effect in 1887[1] scientists had the idea of generating electricity from sunlight. By capturing solar energy and convert it to electric power or use it to produce Hydrogen was a demanding issue. In 1967, discovery of the Honda-Fujishima effect by Akira Fujishima, the photocatalytic properties of Titanium dioxide were popular among physicists as well as chemists. In photovoltaics, the photons which hit the semiconductor, create an electron – hole pair, if this happens at a junction between two different materials (usually this is inorganic salt) this effect will generate an electric potential difference between two phases. The junction between this inorganic solid salt has been doped with silicon.

This silicon doped devices are expensive because they need high temperature and vacuum conditions for the manufacturing process. Fabrication of polymer and nanocrystalline materials is cheaper than conventional silicon devices. It's also flexible and can be shaped to the need. Today, photoelectrochemical devices are produced by replacing the phase in contact with the semiconductor by an electrolyte liquid, gel or organic solid.[1] Development of this type of cells are critical to sustainable future. Energy supply from sun is 4000 times larger than human energy needs. The whole world can be powered by covering the Spain from solar panels with 15% of efficiency. All these reasons make solar cells crucial to sustainable energy.

Regenerative and photosynthetic cells[2]

This paper describes two main types of cells. First type is regenerative cells. This type executes no chemical change and convert light into energy. When the absorbed photon energy is higher than the energy of the band gap, electron-hole pairs will generate. This electron and hole is separated by the electric field present in the "space charge layer". The electron goes through the semiconductor to the external circuit. Hole moved to the surface where they reduced. The oxidized species again reduced back to former reduced species by the electrons which reenter the cell from the external circuit. Most of the regenerative cells are consist with vanadium (II) / vanadium (III), I_2/I^- and sulphide / polysulphide. For multi junctional regenerative cells efficiencies are recorded up to 19.6 % for the study orchestrated by Licht.

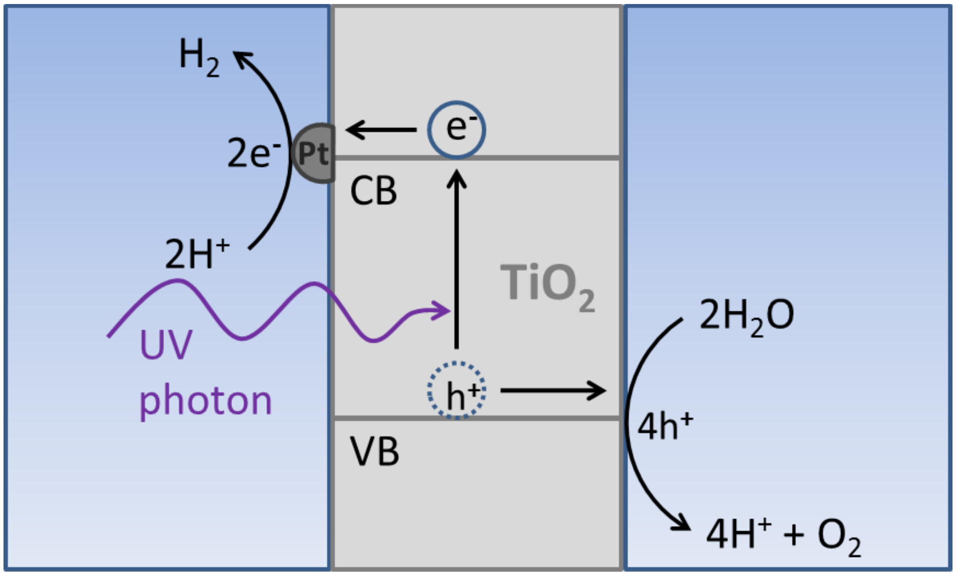

Figure 1: Titanium dioxide photoelectrochemical cell

Second type of the cell has two redox systems.

1) React with holes at the surface of the semiconductor
2) React with the electrons which enter the counter electrode

In the above diagram, explain these two redox systems. At one end (photoanode of the semiconductor) water is oxidized to molecular oxygen while at the other end (photocathode) H^+ is reduced to molecular Hydrogen. The overall reaction is cleavage of water by energy of the sun. So far, TiO_2 and other metal oxides have been successful in these studies. $SrTiO_3$ and $BaTiO_3$ are two prominent examples but there's a drawback due to their efficiencies.[4] Reason for these efficiency is lie on the semiconductor. In the conduction band 3d character is prominent due to Titanium and the valence band has 2p character due to Oxygen. The bands gap between these two bands (3 eV) are wide, therefore it can absorb only UV radiation, resulting low conversion efficiencies.

Changing microstructure to improve the performance (by shifting the band gap to visible region) has been an option for Titanium contain semiconductors. Researches has developed TiO_2 nanowire arrays and porous nanocrystalline so far and these materials are still under examination for photoelectrochemical cells.[5]

Another option is GaN. Nitride is the key for efficient photoelectrochemical effect. Because metal nitrides have a narrow band gap which can include more than 50% of the solar spectrum.[6] Band gap of GaN is narrower than TiO_2 but it's narrow enough to occur the water splitting at the surface. GaN nanowires have better performance due to their large surface area and higher single crystallinity and GaN thin films have low performance due to low crystallinity. GaN nanowires has longer electron – hole pair lifetime due to its high single crystallinity[7].

Non oxide like GaAs, MoS_2, WSe_2 and $MoSe_2$ are used as n – type electrode because they have higher stability in chemical and electrochemical steps in the photocorrosion reactions[8].

Nanocrystalline junctions

Mesoscopic semiconductor materials have gained the attention of the scientific community in the last several years. This is because it has a large internal surface area and it's a systematically structured material. Mesoporous oxide films are thoroughly designed by aligning small crystals in few nanometer distance. There are several suitable compounds for preparing this material. TiO_2, ZnO, SnO_2, Nb_2O_5 and CdSe are some of those. The pores of the mesoscopic materials are filled with semiconducting or conducting material like n-type semiconductor, p-type semiconductor, a polymer, an electrolyte or a hole transmitter. The goal of these material is to make a large surface area which is electronically accessible.[3]

Quantum confinement effects are another interesting feature in nanocrystalline materials. These effects are visible when the films were made out of small quantum dots like CdTe particles. These layers have large band gaps than rest of the material. Because the conduction band redox potential is lowered and valence band is increased resulting an increment of the overall band gap. As a result of this, redox process is feasible where bulk material can proceed.

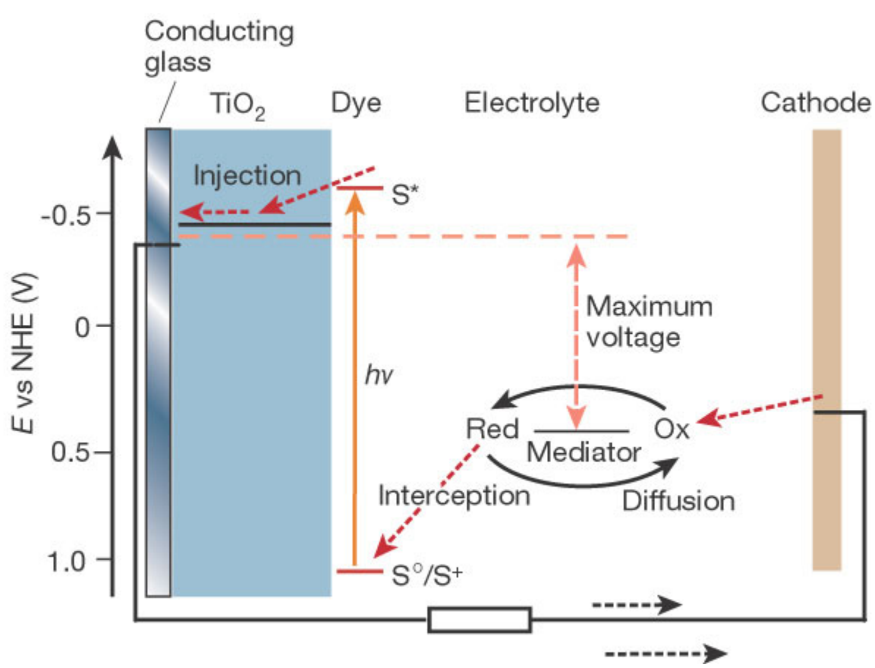

Figure 2: A diagram of dye sensitized electrochemical photovoltaic cell. The photoanode which is made out of mesoporous dye – sensitized semiconductor gets electrons from excited dye. The oxidized dye then oxidizes the mediator which is a redox species in the electrolyte. Mediator will regenerate by using the electrons from cathode; where the cathode gets electrons from the external circuit.

Water splitting by solar energy

The tandem cell is a cell which cleave a water molecule and these cells are based on group III and group V semiconductors. Those type of cells are based on single crystal materials and despite the higher efficiencies those are expensive to manufacture in larger scale.
Low cost tandem devices were developed based on two photosystems connected in series. Usually a nanocrystalline substance (WO_3 or Fe_2O_3) absorbs the blue part of the spectrum. The created holes in the valence band, oxidized water to Oxygen.

$$4h^+ + H_2O \longrightarrow O_2 + 4H^+$$

The electrons in the conduction band are pumped in the next photosystem which has dye sensitized nanocrystalline cell. Second photosystem produce Hydrogen by using conduction band electrons.

$$4H^+ + 4e^- \longrightarrow 2H_2$$

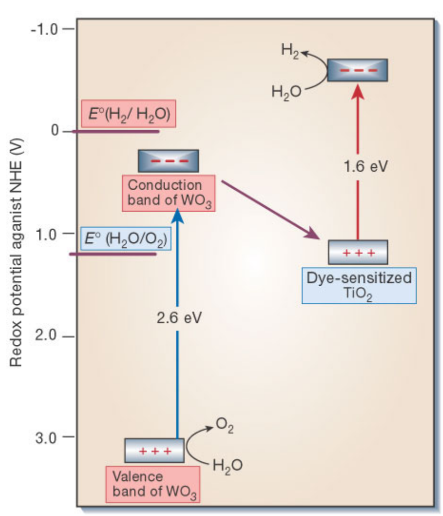

Figure 3: Water splitting by Tandem cell[3]

Overall reaction is splitting up a water molecule by solar radiation. The advantage of the tandem cell is the higher efficiency; this can be achieved by single junction cell but two photosystems must absorb complementary radiation. Still the efficiency of converting solar energy to chemical energy (Hydrogen) is quite low (5 %).

Organic solar cells

These solar cells have few advantages over other inorganic solar cells. Low cost and easy process are few of those. Organic substances can fabricate on different substrates and flexibility of these materials have increased the application. The choice of these material is unlimited and selective absorbtion of solar radiation is possible. Drawback of this system is solar radiation can penetrate the polymer layer without creating potential difference between two layers. Therefore, the efficiency of the system is very low[3].

Conducting polymers like PPV derivatives and C_{60} particles are getting attention as photovoltaic materials. By mixing two organic materials where one is serving as n-type conductor and the other one p-type conductor, hetero junctions can be prepared easily.

Conclusion

Despite the all advantages of the photoelectrochemical solar cells, photovoltaic cells have been more popular in the research community. Following table gives a rough explanation on performance of different types of PV and photoelectrochemical cells. Nanostructured cells exhibit several advantages over other types of solar cells. These cells can produce energy cheaper than silicon cells. Silicon efficiency won't increase with increasing

Table 1: Performance of PV and phototchemical solar cells

Type of cell	Efficiency (%)* Cell	Module	Research and technology needs
Crystalline silicon	24	10–15	Higher production yields, lowering of cost and energy content
Multicrystalline silicon	18	9–12	Lower manufacturing cost and complexity
Amorphous silicon	13	7	Lower production costs, increase production volume and stability
$CuInSe_2$	19	12	Replace indium (too expensive and limited supply), replace CdS window layer, scale up production
Dye-sensitized nanostructured materials	10–11	7	Improve efficiency and high-temperature stability, scale up production
Bipolar AlGaAs/Si photoelectrochemical cells	19–20	—	Reduce materials cost, scale up
Organic solar cells	2–3	—	Improve stability and efficiency

*Efficiency defined as conversion efficiency from solar to electrical power.

temperature, but for nanocrystalline cells the efficiency increases with the temperature. It also has the capability to collect solar energy from all angles. Transparent and colorful panels have made from nanostructured cells. It's the most excited feature than other solar cells. With all these possibilities, there's a wide opportunity to these materials to hit the market in near future.

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