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QUANTUM DOT SOLAR CELL. AN HSAB PERSPECTIVE

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Abstract *The Hard Soft Acid Base (HSAB) theory is presented as a new tool for the design of quantum dot based solar cells comprising TiO_2 / bifunctional linker / quantum dot / p-type semiconducting polymer. Since Ti^{4+} is classified as a hard acid and most of the transition metal semiconductor cations on the surface of the quantum dots are soft acids, the main goal of the discussed approach is to select bifunctional linkers with appropiate anchors for assembling quantum dots onto the surface of titania. A plethora of bifunctional ligands which belong to several classes of organic compounds (amino acids, antibiotics, vitamins, seleno compounds, etc.) are discussed and analysed in terms of the HSAB concept. The functionalization of a p-type semiconducting organic polymer backbone with an HSAB-appropiate anchor for improving the design of polymer - quantum dots hybrid interface in the solar cell structure is also presented.*

Keywords: HSAB (Hard Soft Acid Base) concept, bifunctional ligand, anchor, quantum dots, solar cells

1. Introduction

Hard Soft Acid Base (HSAB) principle was introduced by Ralph Pearson [1] in the early nineteen sixties to explain chemical reactivity of different species, the stability of different complexes, preferences of some compounds to react with other compounds, reactions mechanisms, etc. The principle applies to Lewis acids and bases, a well – known classification, according to which a molecule capable to accept an electron pair is an acid, while a molecule capable to donate it is a base.

Soft acids and soft bases exhibit the following features: strong polarizability, low electronegativity, low or zero oxidation state and large atomic/ionic radius. Examples of soft acids are: CH_3Hg^+, Pt^{2+}, Pd^{2+}, Ag^+, I_2, trinitrobenzene, carbenes, metal atoms, tetracyanoethylene, Au^+, Hg^{2+}, GaI_3, Hg_2^{2+}, Cd^{2+}, BH_3. Examples of soft bases include: benzene, ethylene, R_3P, SCN^-, I^-, RSH, R_2S, R_3As, CO.

By contrast, hard acids and bases tend to have a smaller ionic/atomic radius, high oxidation state, high electronegativity and weak polarizability.

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Examples of hard acids, *inter alia,* include : H^+, Ga^{3+}, Ti^{4+} , In^{3+}, La^{3+}, Na^+, Li^+, $Al^{3+,}$ $AlCl_3$, etc.

Examples of hard bases are: $C_2O_4^{2-}$, HO^-, ROH, H_2O, CO_3^{2-} , PO_4^{3-}, $RCOO^-$, RNH_2, R_2NH, R_3N, etc.

Bordeline types of acid and bases can be also identified. Their characteristics are intermediate between those of hard and soft species.

According to the HSAB principle, a hard acid prefers to bond to a hard base and a soft acid prefers to bond to a soft base. Similarly, a borderline Lewis acid prefers to bond to a borderline Lewis base [2, 3].

The interaction between hard acids and hard bases has an ionogenic character, while the interaction between soft acids and soft bases is predominantly covalent.

Despite of published critical review [4], HSAB theory remains an interesting tool of investigation in many areas of chemistry, such as:

Gas sensing: In the last years, our group employed the HSAB theory when selecting and designing sensing layers for the detection of carbon dioxide [5-18], nitrogen dioxide [19], oxygen [20], and sulphur dioxide [21].

Analytical chemistry: The HSAB concept was shown to be a versatile tool for predicting favorable equilibria in reactions involving cations of transition metals [22].

Adsorbtion phenomena: The adsorption of metal ions onto activated carbons was interpreted in terms of the HSAB concept by Alffara *et al.* [23].

Medicinal chemistry, toxicology: Chelation therapy (the use of EDTA (ethylenediaminetetraacetic acid) in the case of hypercalcemia, for instance) and a lot of medical treatments can be understood in the terms of the HSAB theory [24].

This paper presents how a quantum dot solar cell can be designed by using the HSAB principle.

2. Quantum dots, an emerging idea in manufacturing of the photovoltaic cells

State-of-the-art solar cells are expensive and have a low performance versus price ratio. Therefore, improved efficiency and cheap large scale manufacturing technology for solar cells are needed.

The use of quantum dots in the design of solar cells is a promising solution for obtaining solar cell with high efficiency.

Compared to bulk semiconducting materials, quantum dots exhibit superior properties such as, for instance, band gap tuning.

In addition, they can be synthesized in different shapes, and can be processed with a broad variety of materials such as: cadmium selenide, cadmium sulfide, indium phosphide, etc. [25].

A very common quantum dot solar cell structure consists of TiO_2 (acting as n-type semiconductor) / bifunctional linker (ligand) / quantum dot / p-type semiconducting polymer (**Fig. 1**).

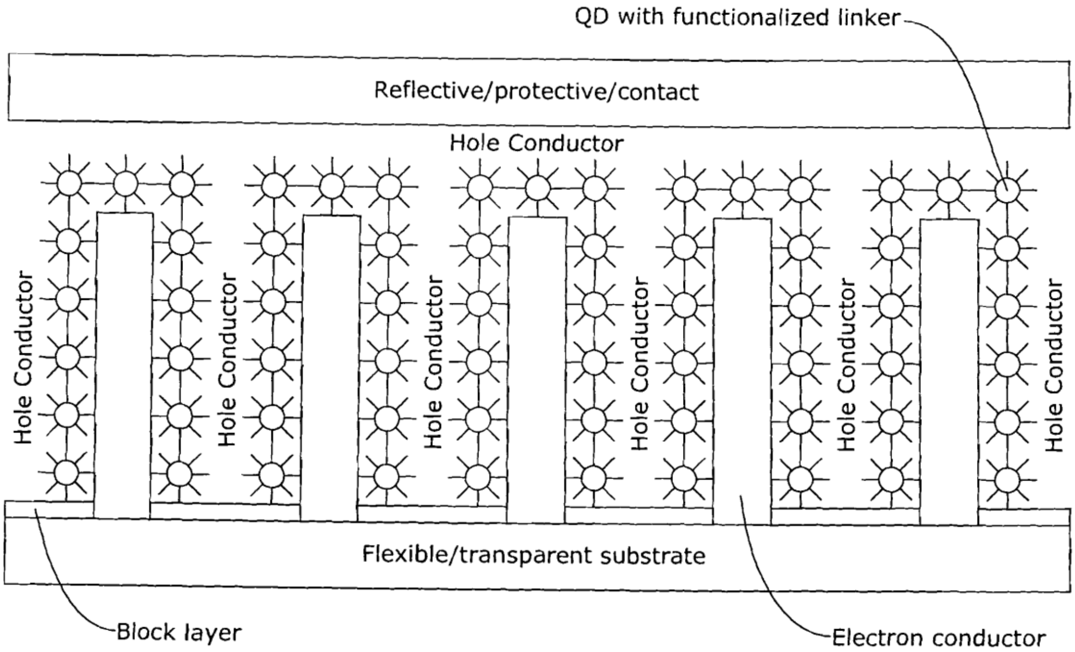

Fig. 1. Schematic cross-sectional side view of an illustrative quantum dot solar cell

When manufacturing such quantum dot solar cells structures, the HSAB principle can be extremely useful when selecting the materials and designing the following interfaces (**Fig. 2**):

Interface 1: TiO_2 - bifunctional linkers (ligands);

Interface 2: Ligands - quantum dots (QDs);

Interface 3: QDs - p-type semiconducting polymer.

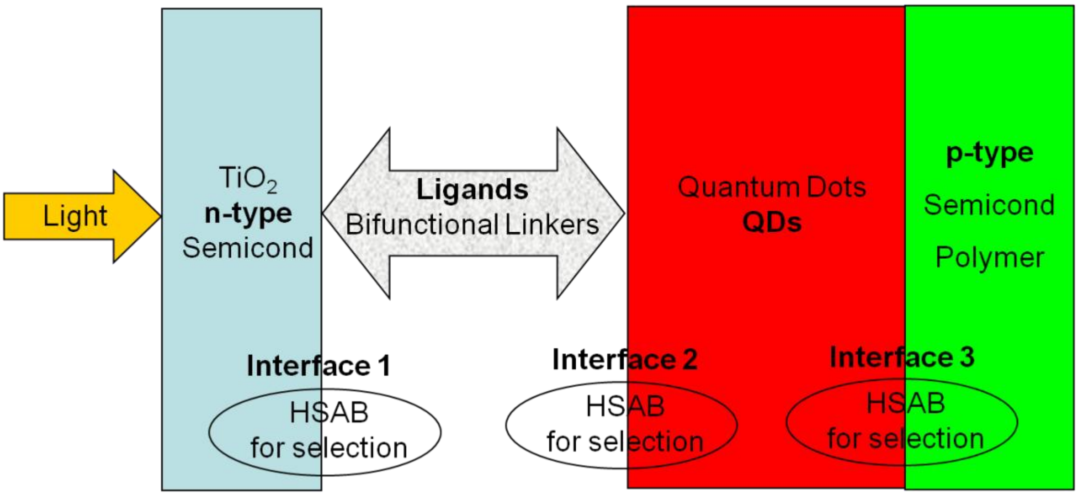

Fig.2. The role of HSAB in the design of quantum dot solar cells.

3. The HSAB principle in modulating the chemical interaction between the TiO_2 layer and the ligand

Usually, bifunctional linkers employ carboxylic acid groups, phosphonic groups, amide, acid chloride or ester groups [26]. For the solar cell quantum dot structure, we propose three ligands as follows: cysteine, homocysteine and isocysteine.

All of the mare are amino acids and amphoteric molecules (as presented in **Fig. 3**).

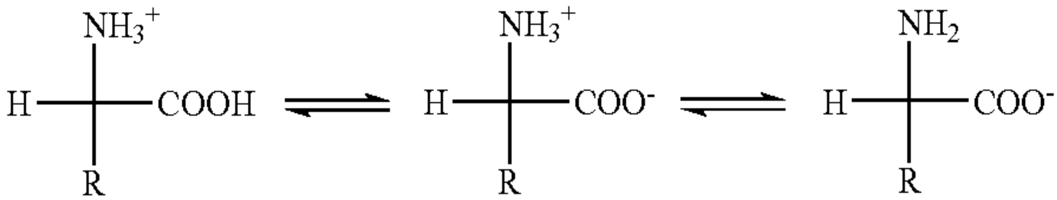

Fig. 3. The zwitterionic character of amino acids

The nature of the TiO_2 - bifunctional linker interaction can be controlled by adjusting the pH of the amino acid solution.

In strong acidic medium (pH < 1), the above selected ligands are mostly in cationic form, thus the deprotonation of the carboxylic group is prevented. A covalent bond may be formed via esterification between the carboxylic group of the amino acids and the oxygen atom in the TiO_2 n-type conducting layer.

In strong basic medium (pH > 12), the ligands are mostly in anionic form and the carboxylic groups are deprotonated (COO^-). The Ti^{4+}, classified as hard acid according to the HSAB principle, is a surface defect in TiO_2 that introduces specific energy levels.

At the same time, the carboxylate group (COO^-) is a hard Lewis base. Therefore, the Ti^{4+}- carboxylate group interaction is a hard acid - hard base interaction and has a pronounced ionogenic character, according to the HSAB theory [27-29].

4. The HSAB principle in modulating the chemical interaction between the ligand and the QDs

According to the HSAB rule, the Cd^{2+}, Cu^+ and Ag^+ cations which can be found at the surface of quantum dots are classified as soft acids. Therefore, they prefer to bond with mercapto group, thioether group, organic sulphides which are soft bases.

CuO, ZnO, Sb_2S_3, Bi_2S_3, PbS and PbSe are other examples of quantum dots that may be employed in the photovoltaic cells discussed herein. Antimony, copper, zinc, bismuth and lead cations are bordeline acids. Therefore, ligands which are bordeline bases can be employed.

Example of suitable bordeline bases include pyridine moieties and arylamine moieties.

As a consequence, the first fundamental step in the functionalization of quantum dots is the selection of either a suitable soft acid - soft base pair or of a bordeline acid – bordeline base tandem, pending on the nature of the QDs. Following this strategy, a series of novel ligands were introduced in the design of quantum dot solar cell structure.

Selenocompounds (such as selenolipoic acid (**Fig. 4**), selenopenicillamine (**Fig. 5**), Se-methylselenocysteine (**Fig. 6**), Se-allylcysteine (**Fig. 7**), selenogluthatione [30]), 2-[2-ethoxycarbonylmethylsulfanyl)ethyl]-1,3-thiazolidine-4-carboxylic acid (**Fig. 8**), 2-acetylamino-3-benzylsulfanyl acetic acid (**Fig. 9**), 2-[(2-oxothiolan-3-yl)carbamoylmethylsulfanyl] propanoic acid (**Fig. 10**), isocysteine [31], vitamins and antagonist of vitamins (such as biotin (**Fig. 11**), norbiotin (**Fig. 12**), homobiotin (**Fig. 13**), actazic acid (**Fig. 14**)), antibiotics (like oxacillin, ampicillin, piperacillin, azlocillin, carbenicillin [32]), contain soft base moieties and can ensure a strong interface with Cd^{2+}, Ag^+, or Cu^+ cations-based quantum dots.

At the same time, all these ligands incorporate one or more carboxyl (-COOH) groups capable to bind to the TiO_2 surface.

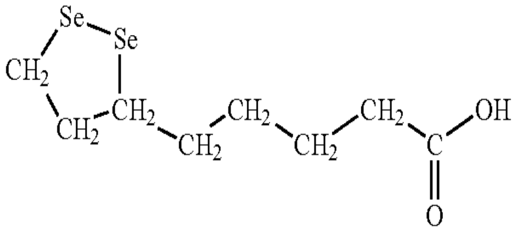

Fig. 4. The structure of selenolipoic acid

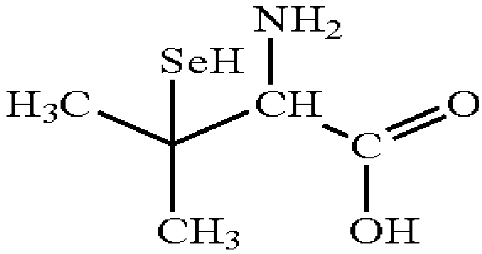

Fig. 5. The structure of selenopenicillamine

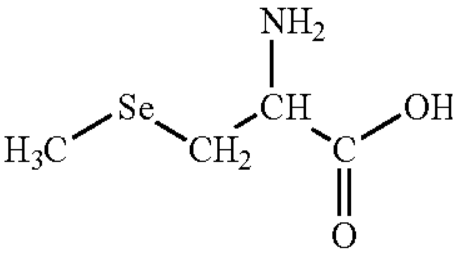

Fig. 6. The structure of Se-methylselenocysteine

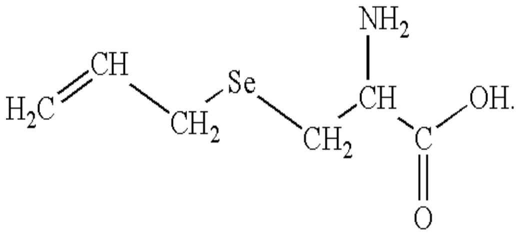

Fig. 7. The structure of Se-allylcysteine

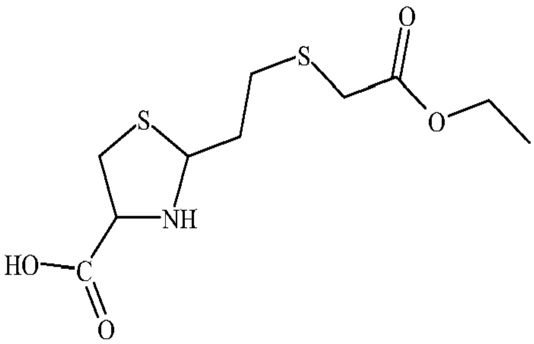

Fig. 8. 2-[2-ethoxycarbonylmethylsulfanyl)ethyl]-1,3-thiazolidine-4-carboxylic acid

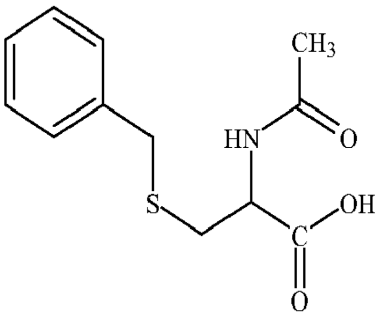

Fig. 9. 2-acetylamino-3-benzylsulfanyl acetic acid

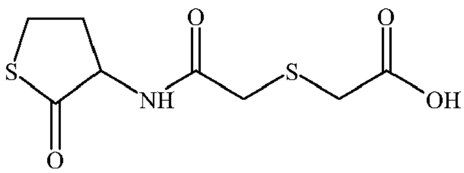

Fig. 10. 2-[(2-oxothiolan-3-yl) carbamoylmethylsulfanyl] propanoic acid

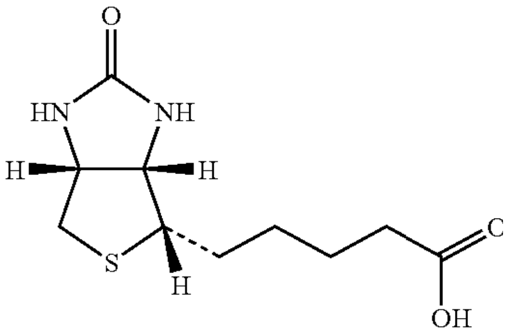

Fig. 11. The structure of biotin

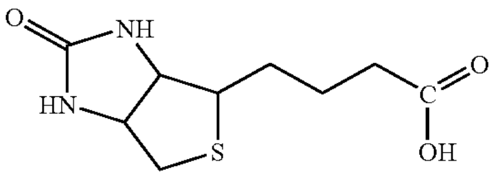

Fig. 12. The structure of norbiotin

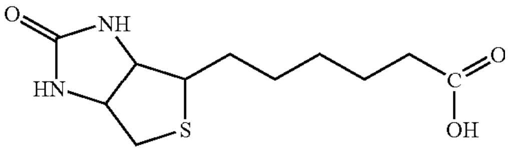

Fig. 13. The structure of homobiotin

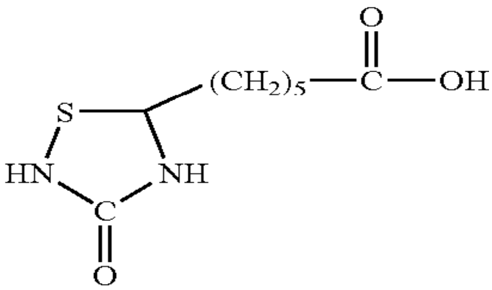

Fig. 14. The structure of actazic acid

5. The HSAB principle in modulating the chemical interaction between the QDs and p-type semiconducting polymers

The power conversion efficiency of different photovoltaic cell structures, including the one presented in this study, is strongly dependent on the charge transfer at the interface between the hybrid quantum dots and the semiconducting organic polymer.

A covalent bond between quantum dots and the polymer increases the charge transfer and the miscibility of the components and avoids seggregation of phases.

To molecularly design the quantum dot - p-type semiconducting polymer interface, the functionalization of polymers with suitable pendant anchors, according to the HSAB theory, can be employed.

For CuO, ZnO, Sb_2S_3, Bi_2S_3, PbS and PbSe – based quantum dots, polythiophene taylored with pyridine group is a suitable p-type semiconducting polymer (**Fig. 15**).

All the above mentioned cations, which are predominatly present at the surface of quantum dots, are classified, according to Pearson's theory, as bordeline acids, while the pyridine group is a bordeline base [33].

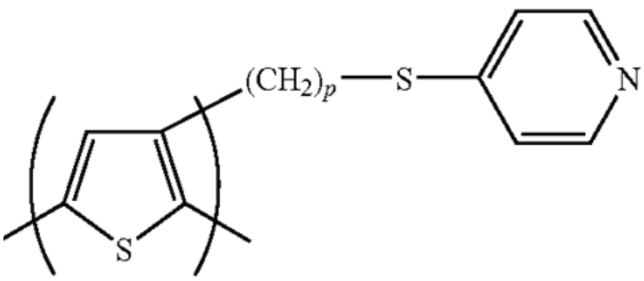

Fig. 15. The structure of polythiophene with pyridine pendant group (p is an integer ranging from 6 to about 12).

At the same time, for CdS, CdTe, CdSe, Ag_2S, PbS – based quantum dots, polythiophene taylored with mercapto group or with thioether group is a suitable p-type semiconducting polymer (**Fig. 16**).

All the above mentioned cations, which are predominatly present at the surface of quantum dots, are classified as soft acids, while the mercapto groups and the thioether groups are soft bases [34-35].

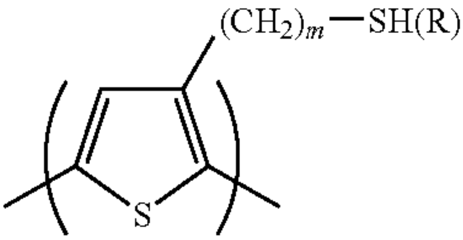

Fig. 16. The structure of polythiophene with mercapto or thioether pendant group (m is an integer ranging from 6 to about 12).

6. Conclusions

The optimization of the design of quantum dot solar cells comprising TiO_2 (n-type semiconductor)/bifunctional linker/quantum dots (light absorber)/ p-type semiconductor polymer was discussed in terms of the HSAB concept.

This concept explains the heuristic approaches in this field. The HSAB theory proved to be higly relevant for selecting the appropriate materials for three types of interfaces: TiO_2 - bifunctional linker, bifunctional linker - quantum dots, and quantum dots - p-type semiconducting polymer.

At the same time, the HSAB theory is a viable tool for the functionalization of the quantum dots and for the design of quantum dots - polymer nanocomposite to be in solar cells and other applications.

Acknowledgment

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