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Hybrid dye sensitized solar cells

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Starting with the nanocrystalline dye sensitized solar cell invented by Graetzel, research in photovoltaics experienced an increased interest by many research teams [1,2]. This paper deals with the synthesis and characterization of new phthalocyanine based chromophores for the fabrication of dye sensitized solar cells and hybrid dye sensitized solar cells. We have synthesized cromophores based on phthalocyanine with different number of pending carboxy groups and utilized them to fabricate solar cells, investigating their photovoltaic response. Based on this, our team developed a hybrid design using polymers obtained by chemical means in the laboratory. As conductive polymers, polyaniline doped with different doping agents and polythiophene were used. For the cell fabrication we have performed the deposition of TiO_2 followed by the dye absorption and the polymer film formation in the case of hybrid cells. The current-voltage characteristic showed the correlation between the structure of the dye and its response. The obtained results showed relative low efficiency similarly to those presented in the literature.

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1. Introduction

One of the major problems of the 21st century is the energetic crisis. If you consider the fact that the energy absorbed by the Earth from the Sun in an hour is sufficient to fulfil the energetic needs of mankind for a year, researchers performed various studies for the manufacture of photovoltaic cells (PV).

Among photovoltaic cells the ones based on dyes represent a relatively more alternative concept than the ones based on p-n junction. The principle of these cells is the following: the dye molecule absorbs a photon and goes to an excited state. From here an electron is injected in the conduction band of a n-type semiconductor (electrode of the cell – TiO_2, ZnO, NiO). The electron follows an external circuit to the counter-electrode of the cell, then it is involved in a redox process and finally it reaches the oxidized dye to regenerate it [1-6].

Photovoltaic cells based on dyes have also some drawbacks than the classical cells. Due to the presence of the electrolyte there are some problems with the sealing of the cell and the electrolyte degradation. The dyes may degrade in time as they are photosensitive elements.

In order to minimize these drawbacks, we have used phthalocyanines-based dyes, zinc carboxy phthalocyanine, which are known for their thermal resistance.[11] Another reason for using this class of compounds is the better anchorage of the dye onto the surface of TiO_2. These dyes also exhibit semiconductive properties characteristic to the phtalocyanines.

In the same time, solid hybrid photocells were obtained where the electrolyte was replaced by electroconductive polymers. For the hybrid cells p-type electroconductive polymers were used to replace the electrolyte. The polymers were polythiophene and polyaniline. To enhance their conductivity several doping methods were used in the research.

2. Materials and methods

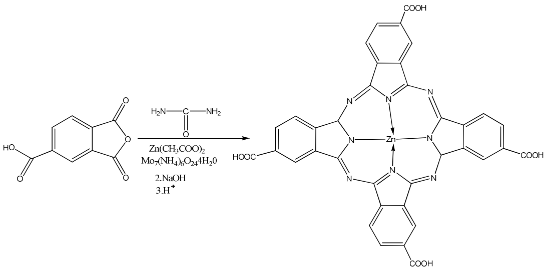
2.1. Materials

Trimellitic anhydride (Merck), urea (Aldrich), ammonium molybdate (Fluka), zinc acetate (Merck), nitrobenzene (Fluka), hydrochloric acid (Merck), sulfuric acid (Merck), methanol (Chimopar), pyromellitic anhydride (Merck), 1,8-diazabicyclo[5.4.0] undec-7-ene (Merck), 2-acrylamido 2-methylpropane sulfonic acid (AMPSA)(Fluka), acetone (Chimopar), ammonia (Chimopar), chloroform (Chimopar), thiophene (T) (Merck), ferric chloride (Chimpar), toluene (Chimopar), dimethylsulfoxide (Fluka), dodecyl mercaptane (Merck), lead acetate (Chimopar), sulfur (Chimopar), ethanol (Chimopar), titanium dioxide (TiO_2) (Degussa P25), acetic acid (Chimopar), Triton X 100 (Merck), dimethylformamide (DMF) (Aldrich) were used as such without any further purification. Aniline (Merck) was purified by vacuum distillation (t=57.9 °C, p=5 mmHg). Potassium persulfate (Aldrich) was recrystallized from an ethanol/water mixture and dried under vacuum.

2.2. Methods

a) Synthesis of zinc tetracarboxy phtalocyanine (Scheme 1)

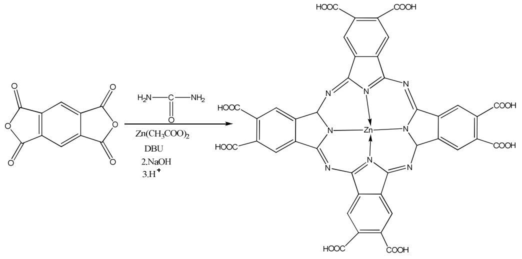
In a three-neck flask equipped with stirrer and thermometer trimellitic anhydride (15 g, 0.078 moles), urea (44 g, 0.73 moles), ammonium molibdate (0.4 g), zinc acetate (3.6 g, 0.0195 moles) and 100 ml of nitrobenzene were added. The mixture was heated at 185°C for 4h. After cooling, 100 ml of water were added and the mixture was stirred at reflux and then filtrated. It was washed with methanol to remove the nitrobenzene traces. The precipitate was added to 250 ml, 10% NaOH solution and it was hydrolyzed for 12h at reflux. It was filtrated hot and the filtrate was acidified with HCl up to positive reaction with Congo red. The precipitate was filtrated and washed with water. For a supplementary purification, the dried product was dissolved in concentrated H_2SO_4 and then it was poured over water.



Scheme 1: Reaction scheme for the Synthesis of ZnPc tetra COOH

b) Synthesis of zinc octacarboxy phtalocyanine (Scheme 2)

In a flask equipped with stirring and condenser pyromellitic anhydride (7.5 g, 0.035 moles), (39 g, 0.66 moles) urea, 1,8-diazabicyclo[5.4.0] undec-7-ene (0.2-0.4 ml) and zinc acetate (8.6 g) were added. The reaction mixture was heated at 250°C for 3h. The reaction product was washed with water, HCl solution (15 ml in 50 ml of H_2O) and was hydrolyzed in basic medium with 10% NaOH solution. Then it was introduced in a flask equipped with stirrer and refrigerant together with 100 ml of 10% NaOH solution and refluxed for 18h, after which it was filtrated. The filtrate was acidified with HCl up to positive reaction with Congo red paper, filtrated and washed with water. For a supplementary purification, the dried product was dissolved in concentrated H_2SO_4 and poured over water.



Scheme 2: Reaction scheme for the synthesis of ZnPc octa COOH.

c) Synthesis of PANI (PANI-ES)

In a 500 ml reactor equipped with stirrer, pouring funnel and thermometer 0.1 moles of fresh distilled aniline were added. The temperature was kept at 0°C. Then 0.1 moles of 35% HCl were added to obtain the aniline clorhydrate. This product is quickly formed as a white-yellow precipitate accompanied by a high volume of HCl vapours. After 45 minutes, 0.1 moles of potassium persulfate in 75 ml of demineralised water were drop added for 60 minutes. A blue precipitate was formed and the reaction mass was kept over night at 0°C. The obtained precipitate was washed with distilled water on the filter paper and dried in vacuum to constant mass. The yield was 80%.

d) Synthesis of PAMPSA

AMPSA (7 g, 0.033 moles) was dissolved in 50 ml of distilled water and potassium persulfate (0.1 g) was added. Nitrogen was bubbled for 10 minutes within the reaction mixture. Then it was placed in a thermostatic bath at 80°C for 5 hours. The polymer was precipitated in acetone, filtrated and dried in vacuum to constant mass.

e) Synthesis of PANI doped with PAMPSA

PAMPSA (5.8 g) was dissolved in 375 ml of distilled water and then aniline (3 ml) was added and stirred for 1 h at room temperature. Separately a solution of potassium persulfate (7.3 g) in 20 ml of distilled water was prepared, and then was added to the initial solution at 0°C. The reaction was kept at this temperature for 6 h, after which the mixture was precipitated in acetone, it was filtrated and the precipitate was dried in vacuum to constant mass.

f) Synthesis PANI - emeraldine base (PANI-EB)

PANI (0.5 g) was added to 100 ml solution of 0.1 M ammonia. The reaction was kept under stirring for 24 h at room temperature. The reaction product was filtrated and dried under vacuum.

g) Synthesis of sulfonated PANI (PANI-SO_3H)

PANI-EB (0.5 g) was added to 40 ml of H_2SO_4. The mixture was stirred for 2 hours at room temperature. Then 200 ml of methanol were drop-added for 20 minutes on an ice bath and finally 100 ml of acetone were added. The precipitate was filtrated and washed with methanol up to pH=7. Finally the product was dried under vacuum to constant mass.

h) Synthesis of PT

60 ml of chloroform were added to 3 ml of thiophene and then 10 g of ferric chloride were introduced in this solution. The mixture is kept under stirring over night. After which it was precipitated in methanol and dried under vacuum to constant mass.

i) Synthesis of PbS in the presence of PT

A mixture of 30 ml of toluene, 10 ml of dimethylsulfoxide, 5 µl of dodecyl mercaptane, 0.1 g of lead acetate and 0.3 g of PT was stirred and heated at

100°C for 20 minutes. 0.1 g sulfur was dissolved in 10 ml of toluene and injected in the first solution. The reaction mixture was kept at the same temperature for 10 minutes, and then it was precipitated in ethanol, filtrated and dried under vacuum to constant mass.

j) Cell set-up

1. Obtaining of TiO_2 paste

2g of TiO_2 were mixed with 1ml of acetic acid solution (pH=3-4) in three portions and the mixture was grinded to obtain a homogeneous paste. Finally Triton X 100 was added as a surfactant.

2. Deposition of TiO_2 layer and sinterization stage

The surface of the conductive glass was covered with TiO_2, the excess being removed by spin-coating technique.

The conductive plate with TiO_2 layer was placed in the oven at 450°C for 30 minutes.

3. Deposition of the dye

The conductive glass with TiO_2 layer was introduced after sinterization in a dye DMF solution ($c=3x10^{-4}$ M). After 24h immersion, the solvent was removed by vacuum evaporation at 80°C.

4. Deposition of polymer film

The polymer film was obtained by solution spin coating. The solvent layer was removed by vacuum evaporation of the plates at 80°C.

5. Closing the cell circuit

For closing the circuit, we may use as counter-electrode the conductive glass (ITO) and to improve the interaction with the electrolyte we use a thin layer of graphite. We have used as electrolyte a solution of KI (0.5M) and I_2 (0.05M) in ethyleneglycol.

2.3. Characterization

FT-IR spectra were recorded with a Bruker Vertex 70 device, domain 400-4000 cm^{-1}, resolution 4 cm^{-1}.

UV-VIS spectra were recorded with an Able Jasco V550 device equipped with an integrating sphere for the film samples.

The crystalline phase of the powder samples was identified by X-ray diffraction (XRD) on a Bruker AXS D8 Advance instrument with Cu Kα radiation ($\lambda = 0.154$ nm). The source was operated at 40kV and 40 mA and the Kβ radiation was eliminated using a nickel filter.

The spin coater used was a TC100 apparatus.

3. Results and discussion

The first approach of this study consists in the characterization of the synthesized dyes both by FT-IR and UV-VIS spectroscopy. The following characteristic peaks (cm^{-1}) could be observed in FT-IR spectra: 3300 (ν_{O-H}), 3103, 3078, 3042 (ν_{C-H}), 1710 ($\nu_{C=O}$), 1654, 1590 (ν_{C-C}), 1484, 1446, 1284, 1173 (δ_{C-O}), 1228, 1088 (δ_{C-H}), 1004, 880, 770, 705, 570, 499, 435. According to literature data [6, 7], the characteristic peaks confirm the synthesis of carboxylic derivatives of zinc phtalocyanine. To confirm this first result, UV spectra were also recorded.

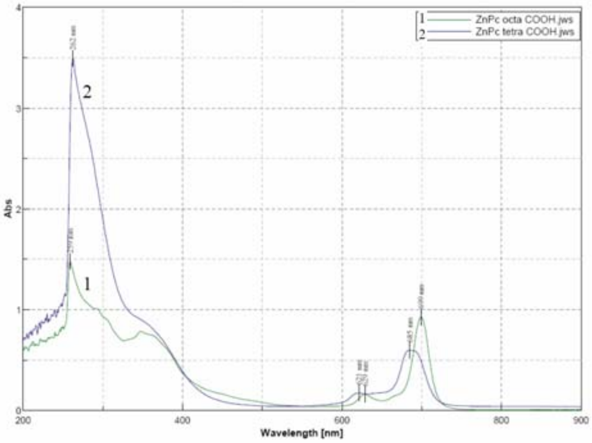


Fig. 1. UV-VIS spectra of the synthesized dyes

UV-VIS spectrum (Fig. 1) shows the characteristic peaks of the phtalocyanines (621 and 685 nm for zinc tetracarboxy phtalocyanine, whereas 629 and 699 nm for octacarboxy phtalocyanine). A strong UV absorption is noticed for both phtalocyanines. The strongest absorption peak assigned is the Q band, which could be attributed to the allowed P-T* transition [10]. All these results confirm the structures of the synthesized dyes (figure 2).

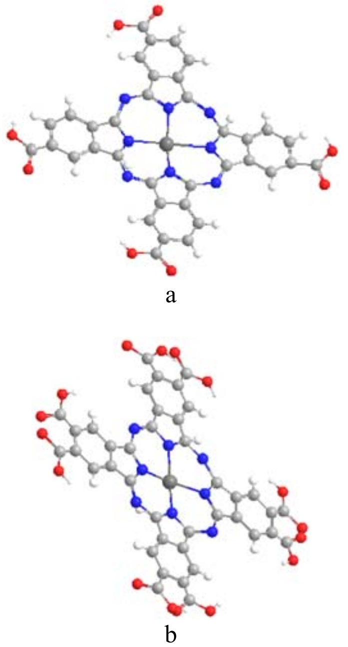


Fig. 2. Structure of zinc tetracarboxy phtalocyanine (a) and zinc octacarboxy phtalocyanine (b)

Next approach consists in the characterization of the conductive polymers. The same spectroscopic methods were used as in the previous case. The following characteristic FT-IR peaks (cm^{-1}) could be assigned in the case of PANI: 3500 ν_{NH2} as vibration, 3400 ν_{NH2} sim, 788 γ_{NH2}, 3005 ν_{CH}, 1500 $\nu_{C=C}$, 863 γ_{CH}. In the case of PANI doped with HCl the characteristic peak is 540 cm^{-1}, as compared to PANI doped with PAMPSA where the characteristic peak is 1735 cm^{-1} specific for $\nu_{C=O}$ (ester group).

UV spectrum for PANI-EB (Fig. 3) shows 2 absorption bands: 634 nm (shifting of the electron from the benzene structure to quinone structure) and 303 nm ($\pi \rightarrow \pi^*$ transition of the benzene ring). In the case of PANI-ES we noticed 3 signals: 790 nm (shifting of the electron from the benzene structure to quinone structure), 393 nm ($\pi \rightarrow \pi^*$ transition of the benzene ring) and 260 nm ($\pi \rightarrow \pi^*$ electron jump of C=N). [13,14].

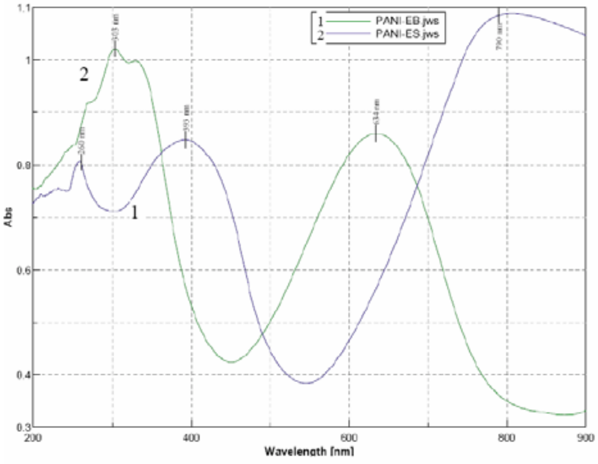
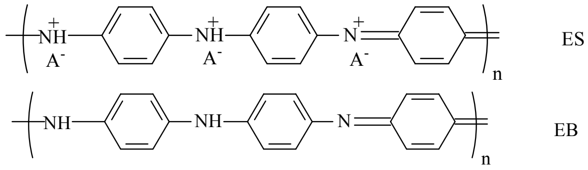


Fig. 3. UV-VIS spectra for PANI-EB and PANI-ES



Scheme 3: Structures of PANI-ES and PANI-EB

Fig. 4 shows the peaks from 628.68 cm^{-1} specific to $\nu_{S\text{-}O}$ and 1188.11 cm^{-1} specific to ν_{SO2as}. These bands confirm the structure of PANI-SO_3H.

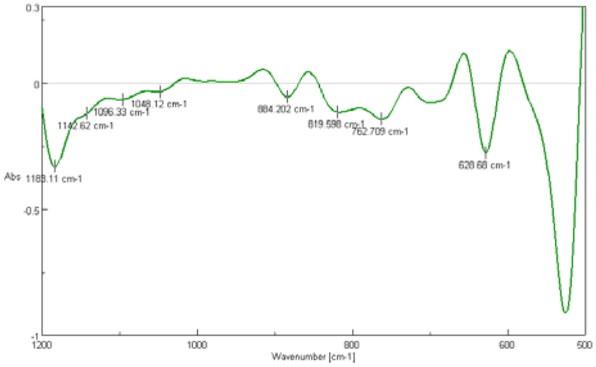


Fig. 4. FT-IR spectrum of PANI-SO_3H

FT-IR spectrum of PT shows the signals at 3100 cm^{-1} characteristic to ν_{CH}, 1500 cm^{-1} specific to $\nu_{C=C}$ and 700 cm^{-1} specific to γ_{CH}. UV spectrum (figure 5) reveals peaks at 271 nm ($\pi \rightarrow \pi^*$ transition of the cyclopentadiene ring) and 297 nm ($n \rightarrow \pi^*$ transition of the un-paired electrons of the S atom).

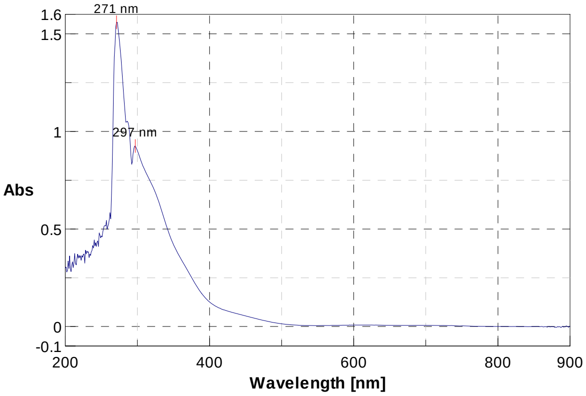
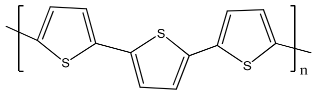


Fig 5. UV-VIS spectrum of PT.



Scheme 4: Structure of PT

For the characterization of PT doped with PbS there were recorded various X-ray diffraction spectra shown in Fig. 6. The peaks with 2θ values of 26.0, 30.1, 43.1, 51.0, 53.5, 62.6, 68.9, 70.9 and 79.0 correspond to the crystal planes (111), (200), (220), (311), (222), (400), (331), (420) and (422), which may be indexed to the pure cubic phase for PbS (JCPDF card no. 5-0592). The strong and sharp diffraction peaks suggest that the PbS is well crystallized.

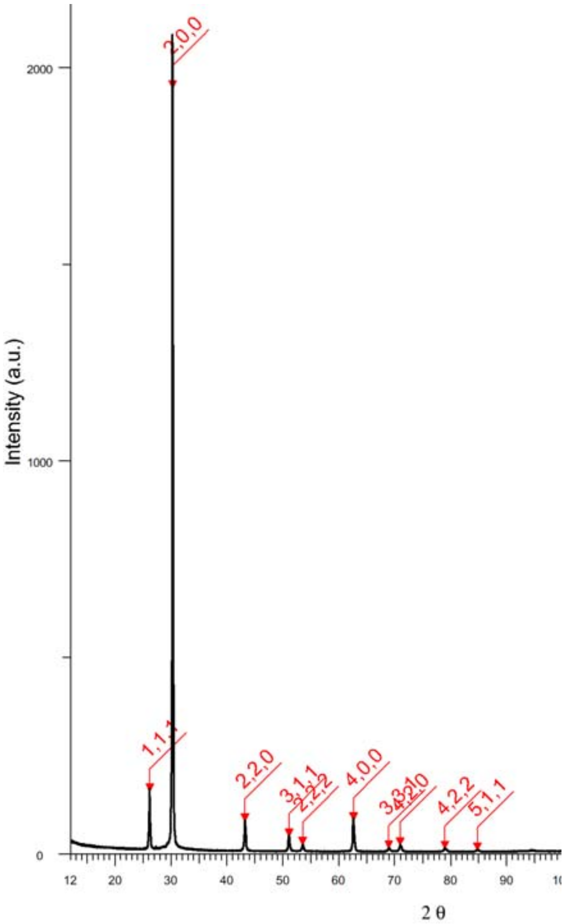


Fig 6. X-ray diffraction spectrum of PbS generated in the presence of PT

The synthesis of PbS in the presence of PT followed the increase of quantic efficiency of the cell, knowing that PbS has excellent semiconductor properties at nanometric level. Additionally, it has advantageous properties like solar spectrum matching, multiple electron hole generation ability and tailor made which make them suitable candidate as a sensitizer/co-sensitizer in solar cells [7, 8]. A quantum dot is a granule of a semiconductor material whose size is on the nanometer scale. These nanocrystallites behave essentially as a 3-dimensional potential well for electrons (i.e., the quantum mechanical “particle in a box”) [9].

The reflectance of the films was measured and then it was converted into absorption to compare it with the spectra of the dyes in solution. UV-VIS spectra (figure 7) of the TiO_2 films with different dyes reveal a stronger absorption in the case of ZnPc octa COOH due to its higher concentration on the TiO_2 layer. This behaviour could be explained by the enhanced ability of this dye to anchor onto the TiO_2 layer with the carboxyl groups [12].

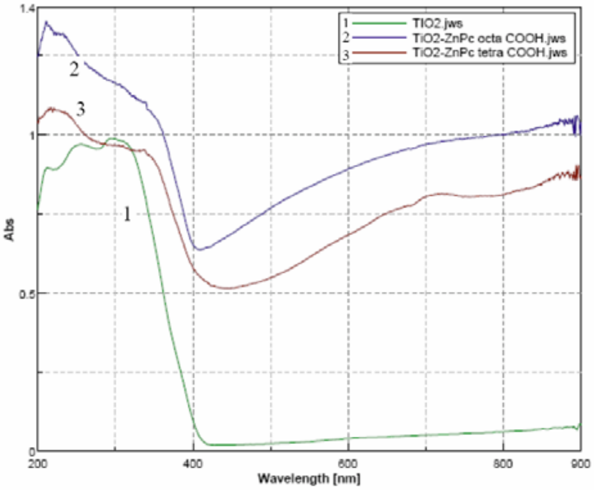


Fig .7. UV-VIS spectrum of dye films on TiO_2

The influence of the polymer film on the absorption was evaluated by UV-VIS spectra of the films TiO_2/dye/polymer (Fig. 8). The minimum influence of the polymer upon the dye absorption in the visible spectrum is observed.

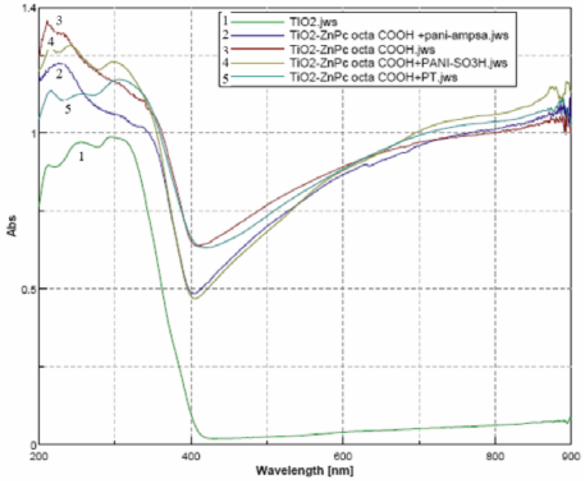
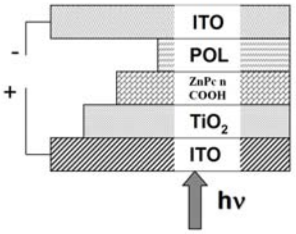


Fig. 8. UV-VIS absorption spectrum of films TiO_2/dye/polymer

Next step, after the characterization of the compounds for the solar cell, consists in the manufacture of the solar cells and measuring their properties. The set up scheme is shown in scheme 5.



Scheme 5: Set up of the solar cell

The cell parameters vary with the polymer used and the values are presented in Table 1.

Table 1. Voltage and intensity of the solar cells measured at light intensity of 100mW/cm^2.

Symbol	Cell	Voltage (mV)	Intensity (μA)
C1	ITO+TiO_2 + 4 COOH ZnPc+ electrolyte of I_2/KI + Graphite	178	3.6
C2	ITO+TiO_2 + 8COOH ZnPc+ electrolyte of I_2/KI + Graphite	256	5.1
C3	ITO+TiO_2 + 8COOH + PT + ITO	0.2	0.01
C4	ITO+TiO_2 + 8COOH + PT + electrolyte of I_2/KI+ ITO	4.2	1.2
C5	ITO+TiO_2 + 8COOH + PT/PbS+ ITO	35	0.3
C6	ITO+TiO_2 + 8COOH + PANI/PAMPSA+ ITO	38	0.01
C7	ITO+TiO_2 + 8COOH + PANI-SO3H+ ITO	20	0.01

The data from this table could be analyzed in a comparative manner and they show an increase both of the intensity and voltage in the case of 8COOH ZnPc. This could be explained, on one hand, by the high concentration of the sensitizer due to a good anchorage on the TiO_2 layer (high intensity) and, on the other hand by a stronger energetic difference between the energetic level of the excited stare and the conduction band of TiO_2 (high voltage). This fact led to the use of this dye to manufacture the new hybrid cells. Comparing the values for C3 and C4 we may notice the increase of the efficiency when using the classic electrolyte. This is explained by the improvement of the regeneration ability of the polymer through charge carriers with high mobility. In the case of quantum dots (C5) we may notice the increase of the efficiency when using PbS nanoparticles. In the case of C6 and C7 the voltage is increased by using PANI-PAMPSA.

4. Conclusions

A research study concerning the manufacture of new hybrid dye sensitized solar cells was realized. The influence of the functional groups upon the anchorage of the dye on the TiO_2 layer was established. The structure of the conductive polymers for the hybrid cells was confirmed by UV-VIS, FT-IR and X-ray diffraction techniques. The dye absorption is poorly influenced by the polymer film. The performance of the hybrid cells is promising with doped PANI and PT-PbS (quantum dots).

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