Gold nanoparticles bind to porphyrins. A potential dye-sensitized solar cell

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Abstract. Porphyrins could be used for designing dye sensitized solar cells. The correlation between their band gap HOMO-LUMO and the conduction band of the semiconductor (TiO$_2$) allows the electron transfer from the dye to the electrode, through the semiconductor. Our work reported here has revealed that a strong and large absorption band is obtained when a complex between gold nanoparticles (GNP) and porphyrin dye is formed.

1. Introduction
As a renewable alternative energy source, solar energy is a potential choice for solving the shortage of fossil energy. In this regard, solar cells could convert solar energy into electric power. Currently, the most popular methods are silicon based solar cells.

The production of electrical power from sunlight in organic solar cells involves the following: firstly, sunlight photons are absorbed within a photoactive layer leading to the formation of excitons. The excitons migrate to the interface of a donor-acceptor semiconductor hetero-junction and dissociate to form free charges, consisting of electrons and holes, and these charges are moved to the electrodes to eventually yield a photocurrent in an external circuit.

Dye-sensitized solar cells have many advantages over the conventional silicon solar cells [1]. These cells work on principles similar to the processes in natural photosynthesis. They use an organic dye to absorb the incoming light and produce excited electrons which will generate electrical current. The absorption band of the dye has to be as large as possible, from 350 nm to 900 nm, in the visible and near-infrared region of the solar spectrum. TiO$_2$-Ru dye sensitized based on solar cells have limited availability and undesirable environmental impact, due to Ru atoms. These facts led to search for cheaper and safer organic-based dyes. Given their efficacy in photosynthesis, porphyrin dyes have great potential in this regard [2-4].

In this work, we investigate the coupling between gold nanoparticles and porphyrins, and these new materials will be helpful to the design of dye sensitized solar cells (DSSE).

2. Experimental

2.1. Materials and methods
Hydrogen tetrachloroaurate (HAuCl$_4$·3H$_2$O) was purchased from the Institute of Chemistry in Cluj-Napoca, whereas sodium citrate, dichloromethane and tetrabutylammonium perchlorate
from Sigma Chemie GmbH Germany. The porphyrin dye ZnP:Zn(II)-tetrapyridylporphyrin was synthesized at the Institute of Chemistry, in Timisoara. OEP: 2,3,7,8,12,13,17,18-octaethylporphyrin was purchased from Aldrich. Double distilled water was used in all experiments.

UV-Vis and fluorescence spectroscopic studies were carried out using a Jasco 550 and Jasco FP-6500. Gold nanoparticles were prepared using Turkevich method [5]. TEM images (using a JEOL JEM 1010 Transmission Microscope) demonstrated that we have obtained 30 nm gold nanoparticles.

2.2. Discussion and results

After dissolving the porphyrin molecules in dichloromethane, we acquired the absorption spectra of these dyes. The porphyrin dyes have an intense and narrow absorption band at 420 nm (Soret band) and a large, weak band between 500-700 nm (Q band), as seen in figure 1.

![Absorption spectra of porphyrins](image)

**Figure 1.** UV-Vis spectra of porphyrins: a) the entire spectra, b) Q band of porphyrins.

Analising the Soret band, with the \( \lambda \)-onset method, we determinate the energy gap between HOMO and LUMO (\( \Delta E_g \)). Using cyclic voltammetry we obtained the electrochemical spectra of the porphyrins (figure 2), solved in dichloromethane.

![Cyclic voltammogram of OEP](image)

**Figure 2.** Cyclic voltammogram of OEP.
An Ag wire was used as reference electrode. From the cyclic voltammogram, we calculated the redox potential $E_0$. A conversion was made to NHE. With $\Delta E_g$ and $E_0$ known, it is possible to determine the energy levels HOMO and LUMO, and to compare them with the levels of the semiconductor (TiO$_2$). The results are shown in table 1.

Table 1. $E_0$, HOMO, LUMO for porphyrins, TiO$_2$ and electrolyte, with NHE reference.

| Porphyrin | $\lambda$ onset (nm) | $\Delta E_g$ (eV) | $E_0$ (eV) | HOMO (eV) | LUMO (eV) (conduction band) |
|-----------|----------------------|------------------|-----------|----------|-----------------------------|
| ZnP       | 469                  | 2.64             | -         | -        | -                           |
| OEP       | 423                  | 2.93             | 0.972     | 0.972    | -1.958                      |
| TiO$_2$   | -                    | 3.20             | -         | 3.000    | -0.200                      |
| Electrolyte| -                    | -                | 0.300     | -        | -                           |

To design dye-sensitized solar cells, it is necessary that the dye absorb the visible light and then transfer the photoelectron from his LUMO state to the semiconductor. This orbital must have a higher energy than the conduction band of the semiconductor, so the electron could pass to the semiconductor and then from the electrode, in the external circuit. Also, HOMO energy level of the dye must be lower than the redox potential of the electrolyte.

As can be seen in table 1 (with NHE reference), LUMO energy state of OEP has a higher value than the conduction band of TiO$_2$, which means that the electronic transfer between dye and semiconductor could happen. Also, the value of redox potential of the electrolyte ($E_0$) is higher than the corresponding values of the dyes and this facilitate the electron transfer to the oxidized dye.

One way to encompass a broader absorption band is the attachment of functional groups on the basis of porphyrins. However this action involves organic synthesis. Gold colloids bearing surface negative charge readily bind the functional groups. This negative charge must be compensated by adding an acidic solution. These conditions facilitate functionalization and linking of GNP to nitrogen atoms in the porphyrinic structure.

The influence of pH on the reaction between GNP and porphyrins was investigated. There is no shift in the maximum peak position in the UV-Vis absorption spectra of gold nanoparticles until the pH value is 2.5. Our experiments were made at pH = 2.52 and the porphyrin we used was ZnP. In figure 3 is presented the UV-Vis spectra for GNP and the sequential addition of ZnP, with modified pH. One can see that the plasmon surface peak of GNP in figure 3a is attenuated and a signal for the newly formed complexes appear between 500-700 nm. When we mixed a fixed quantity of porphyrin solution with GNP, by adding small drops of the GNP solution, the spectra in figure 3b demonstrate that GNP bind to the porphyrinic ring, as a shift appears in the maximum peak position.

Figure 3. UV-Vis absorption spectra of: a) GNP+ZnP$_{drops}$; b) ZnP+GNP$_{drops}$.
This could be due to the existence in the porphyrinic ring of GNP. Metal atoms in the porphyrinic ring are decisive for the lifetime of the electronic excited states, which influence the electron transfer between the dye and the conduction band of TiO$_2$. Zn porphyrins are more efficient than Cu porphyrins for solar cells because they have a longer lifetime of the electronic excited states [2].

3. Conclusion
In this work we demonstrated that porphyrins could be used for TiO$_2$ sensitization. An electronic transfer from the porphyrinic dye to TiO$_2$ is possible due to their HOMO-LUMO energy states. We also proved that some porphyrins capture in the porphyrinic ring gold nanoparticles, and a strong and large absorption band is obtained when a complex between gold nanoparticles and porphyrin dye is formed. This suggests that these structures (porphyrin + gold nanoparticles + TiO$_2$) could be used as new materials for photovoltaic cells.

References
[1] Gratzel M 2001 Nature 414 338
[2] Campbell W M, Burel A K, Officer D and Jolley K W 2004 Coord. Chem. Rev. 248 1363
[3] Gervaldo M, Fungo F, Durantini E N, Silber J J, Sereno L and Otero L 2005 J. Phys. Chem. B 109 20953
[4] Fish J R, Kubaszewski E, Peat A, Malinski T, Kaczor J, Kus P and Czuchajowski L 1992 Chem. Mater. 4 795
[5] Turkevich J, Stevenson P C and Hillier J 1951 Faraday Discuss. II 55.