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ON THE THICKNESS LIMIT OF THE ADSORBED DYE MOLECULES LAYER ON TiO_2 SURFACE

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Dye sensitized solar cells have a thin layer of porous titania on top of which a much thinner film of dye molecules is adsorbed. Although a monolayer of dye molecules provides the maximum efficiency of the device, in practice the dye film happens to be multilayer. Using the well known van der Waals interaction potential the model presented in this paper shows that there is a critical (limit) thickness of dye adsorbed film that depends on the nature of the liquid the dye molecules are solved in.

Keywords: dye synthesized solar cells, TiO_2, dye adsorption

1. Introduction

The global power consumption at the beginning of the actual century was about 13 TW and, considering the growth rate of the population, the annual demand at the level of 2050 is estimated to reach a mean value of 28 TW. [1, 2]. The use of fossil fuels, on which is mainly based the present energy system, is leading to the extinction of its reserves in the next few decades and, moreover, have a significant negative environmental impact. Given these problems, it is a necessity to provide renewable and nonpolluting energy sources able to replace the conventional supplies.

Among the clean sources of energy the solar one is considered the most important. The first devices that used sun's light to convert it in electricity were based on silicon technology [3]. Although in the last fifty years the silicon based solar cells has reached almost the theoretical efficiency, the overall costs remain very high, so these cells are not yet desired economically.

Titania (TiO_2) is a cheap and non polluting semiconductor that can be easily obtained as nanoporous films, but the efficiency of the devices made out of TiO_2 is rather small. One of the main problems with titania was that it is a large forbidden band semiconductor such that only a small part of the solar radiation can be used. At the end of the century, M. Grätzel's group suggested the use of dye molecules that can absorb a light quantum promoting one electron in an excited state (LUMO) that, in turn, having an energy higher than the Fermi level of TiO_2 semiconductor, is injected into the titania and then in the external circuit [4-5]. Grätzel's procedure is known as

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dye sensitized solar cell (DSSC) and represents a promising approach towards clean and cheap energy. Some problems still remain to be solved and one of them is the adsorption of dye molecules inside the porous titania. In this paper the process of adsorption is discussed and practical conclusions are presented.

2. Model

The dye adsorption on TiO_2 surface is very important in order to increase the efficiency of dye-sensitized solar cells (DSSC) as it is the dye that, being excited with visible light radiation, transfers electrons to the adsorbing substrate. The dye molecules are regenerated by the direct contact with the electrolyte that contains the I^-/I^{3-} redox couple. Theoretical models on the charge transfer at dye/electrolyte/TiO_2 mainly consider the adsorption of a monomolecular layer of dye. Multiple molecular dye layers may lead to a decrease in the likelihood of electron transfer to the TiO_2 film as well as to an increase in the probability that the dye molecules are desorbed due to repulsive interactions generated within the system [6-12].

Let us consider the system reported in Fig. 1 containing three media. A solid substrate 1 is in contact with the solvent containing the dye molecules 3 and a thin film of dye absorbed molecules 2 is formed on the solid surface. To estimate the thickness of this film, the total van der Waals interaction energy between one dye molecule placed at distance *h* from the dye substrate and all the other molecules within the three media is evaluated. To estimate the thickness limit of the adsorbed dye film on TiO_2 surface, we evaluate the total van der Waals interaction energy between one dye molecule placed at distance *h* from the dye film and molecules within the 1, 2, and 3 media.Considering the dispersion and polarization interactions entering in van der Waals potential for neutral molecules (or nanoparticles) proportional to r^{-6}, the total interaction energy of a dye molecule, located at a distance $z=h$, away from the interface between 2 and 3 media, with molecules from 1, 2 and 3 is [13]

$$u = u_1 + u_2 + u_3. \tag{1}$$

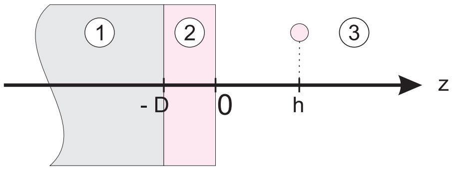


Fig. 1 The solid substrate (1), the film of adsorbed dye molecules (2), and the solvent in which the dye molecules lie (3).

To evaluate this energy we consider that van der Waals interaction potential is purely attractive and the interactions are additive (i.e. the interaction between one molecule and a plane surface of a solid made out of identical molecules is the sum of its interaction with all the molecules of the solid).

Let us first evaluate u_3, representing the interaction of a dye molecule with solvent in which it lies. The dye molecule is approximated with a sphere of radius σ (the Van der Waals packing radius), where σ is a parameter defining the closest approach between two molecules. Hence, the van der Waals interaction energy can be written as

$$w_3 = \begin{cases} 0, & r < \sigma \\ -\dfrac{k_3}{r^6}, & r > \sigma \end{cases} . \tag{2}$$

where k_3 is the interaction constant.

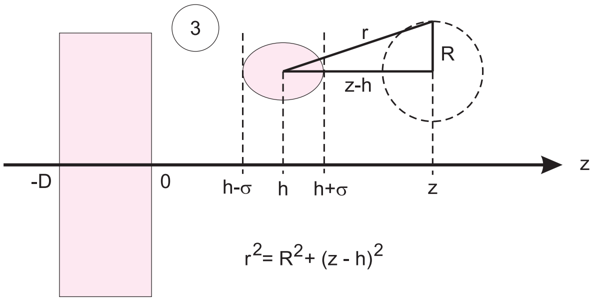


Fig. 2 A dye molecule (pink) in solvent with the van der Waals radius σ interacting to other molecules at distance *r*.

According to Fig.2, u$_3$ energy has three terms

$$u_3 = u_3(z > h + \sigma) + u_3(h - \sigma < z < h + \sigma) + u_3(z < h - \sigma). \tag{3}$$

To evaluate the total interaction energy of the system, cylindrical coordinates are used. We consider the molecules in a circular ring with the transversal section area *dz dR* and radius *R* as shown in Fig.3. The volume of the ring is

$$dV = 2\pi R\, dR\, dz, \tag{4}$$

and the number of molecules within the ring is

$$dN_m = 2\pi\rho_3 R\, dR\, dz, \tag{5}$$

where ρ_3 is the number density of molecules in the medium (3).

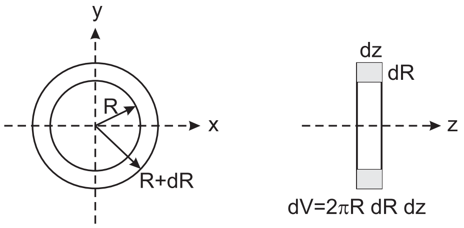


Fig. 3 The circular ring with cross area *dRdz*.

To evaluate u_3 we consider the following terms;

a) $z > h + \sigma$

$$u_3\left(z > h+\sigma\right) = \int_{h+\sigma}^{\infty} dz \int_{0}^{\infty} -\frac{\rho_3 k_3}{\left[R^2+\left(z-h\right)^2\right]^3} 2\pi R dR =$$

$$= -\pi \rho_3 k_3 \int_{h+\sigma}^{\infty} dz \int_{0}^{\infty} \frac{dR^2}{\left[R^2+\left(z-h\right)^2\right]^3} ; \quad \int_{0}^{\infty} \frac{dR^2}{\left[R^2+\left(z-h\right)^2\right]^3} = \frac{1}{2\left(z-h\right)^4} \tag{6}$$

$$u_3\left(z > h+\sigma\right) = -\frac{\pi}{2}\rho_3 k_3 \int_{h+\sigma}^{\infty} \frac{dz}{2\left(z-h\right)^4} = -\frac{\pi}{6}\frac{\rho_3 k_3}{\sigma^3}.$$

b) $h - \sigma < z < h + \sigma$

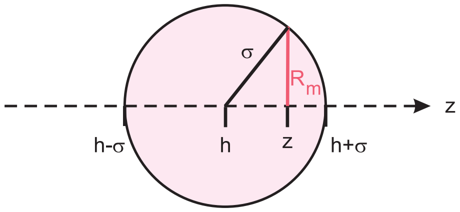
$$u_3\left(h-\sigma < z < h+\sigma\right) = \int_{h-\sigma}^{h+\sigma} dz \int_{R_m}^{\infty} -\frac{\rho_3 k_3}{\left[R^2+\left(z-h\right)^2\right]^3} 2\pi R dR =$$

$$= -\pi \rho_3 k_3 \int_{h-\sigma}^{h+\sigma} dz \int_{R_m}^{\infty} \frac{dR^2}{\left[R^2+\left(z-h\right)^2\right]^3} = -\frac{\pi}{2}\rho_3 k_3 \int_{h-\sigma}^{h+\sigma} \frac{1}{\left[R_m^2+\left(z-h\right)^2\right]^2} dz; \tag{7}$$

$$R_m^2 = \sigma^2 - \left(z-h\right)^2 \Rightarrow \left[R_m^2+\left(z-h\right)^2\right]^2 = \sigma^4;$$

$$u_3\left(h-\sigma < z < h+\sigma\right) = -\frac{\pi}{2}\rho_3 k_3 \int_{h-\sigma}^{h+\sigma} \frac{dz}{\sigma^4} = -\frac{\pi \rho_3 k_3}{\sigma^3}.$$

In step b) the notations described in Fig.4 have been used.



$$R_m^2 = \sigma^2 - (z-h)^2$$

Fig. 4 Coordinates used for a molecule placed at *h*.

c) $0<z<h-\sigma$

$$u_3\left(0<z<h-\sigma\right)=\int_0^{h-\sigma}dz\int_0^{\infty}-\frac{\rho_3 k_3}{\left[R^2+\left(z-h\right)^2\right]^3}2\pi R dR=$$

$$=-\pi\ \rho_3 k_3\int_0^{h-\sigma}dz\int_0^{\infty}\frac{dR^2}{\left[R^2+\left(z-h\right)^2\right]^3}=-\frac{\pi}{2}\rho_3 k_3\int_0^{h-\sigma}\frac{1}{2\left(z-h\right)^4}dz= \tag{8}$$

$$=-\frac{\pi}{2}\rho_3 k_3\left[-\frac{1}{3\ h^3}+\frac{1}{3\ \sigma^3}\right]=-\frac{\pi}{6}\rho_3 k_3\left(\frac{1}{\sigma^3}-\frac{1}{h^3}\right).$$

Summing the steps a), b) and c) up we have

$$u_3=-\frac{4}{3}\pi\frac{\rho_3 k_3}{\sigma^3}+\frac{\pi}{6}\frac{\rho_3 k_3}{h^3}. \tag{9}$$

Inspecting equation (9) we see the interaction of dye molecules in the medium 3 has an r^{-3} dependence on distance. The energy has an attractive term dependent on the sphere radius σ and a repulsive term that depends on the distance from the dye molecule and the dye film already adsorbed on the solid surface.

In the following evaluation of u_2 and u_1, we assume that the Van der Waals energies, connected to the interactions between the dye molecule in solvent with molecules from the 2 and 1 media, are similar to the one described by equation 1 (with the related interaction constants k_2 and k_1) and that the corresponding number density of molecules in each medium are ρ_2 and ρ_1 respectively.

The term u_2 contains the interaction between the dye molecule in a solvent, located at h, and the dye molecules already adsorbed on the solid surface.

$$u_2=\int_{-D}^{0}dz\int_0^{\infty}-\frac{\rho_2 k_2}{\left[R^2+\left(z-h\right)^2\right]^3}2\pi R dR=-\pi\ \ \rho_2 k_2\int_{-D}^{0}dz\int_0^{\infty}\frac{dR^2}{\left[R^2+\left(z-h\right)^2\right]^3}= \tag{10}$$

$$=-\ \frac{\pi}{2}\rho_2 k_2\int_{-D}^{0}\frac{dz}{\left(z-h\right)^4}=-\frac{\pi}{6}\ \ \rho_2 k_2\ \left(\frac{1}{h^3}-\frac{1}{\left(D+h\right)^3}\right)$$

The equation (10) contains two terms that depend on the distance from the dye molecule to the already adsorbed film and on the thickness of this film, respectively.

The last term of the system total energy refers to the interaction of a dye molecule with the TiO$_2$ film.

$$u_1 = \int_{-\infty}^{-D} dz \int_0^{\infty} -\frac{\rho_1 k_1}{\left[R^2 + (z-h)^2\right]^3} 2\pi R dR = -\pi \rho_1 k_1 \int_{-\infty}^{-D} dz \int_0^{\infty} \frac{dR^2}{\left[R^2 + (z-h)^2\right]^3} =$$
$$= -\frac{\pi}{2} \rho_1 k_1 \int_{-\infty}^{-D} \frac{dz}{(z-h)^4} = -\frac{\pi}{6} \rho_1 k_1 \frac{1}{(D+h)^3}. \tag{11}$$

Adding the three energy terms:

$$u(h) = u_1(h) + u_2(h) + u_3(h)$$
$$u(h) = -\frac{\pi}{6} k_1 \rho_1 \frac{1}{(D+h)^3} - \frac{\pi}{6} k_2 \rho_2 \left(\frac{1}{h^3} - \frac{1}{(D+h)^3} \right) - \frac{4}{3} \pi \frac{k_3 \rho_3}{\sigma^3} + \frac{\pi}{6} \frac{k_3 \rho_3}{h^3} \tag{12}$$
$$= -\frac{\pi}{6} \left(\frac{k_1 \rho_1 - k_2 \rho_2}{(D+h)^3} + \frac{k_2 \rho_2 - k_3 \rho_3}{h^3} \right) - \frac{4}{3} \pi \frac{k_3 \rho_3}{\sigma^3}.$$

The total interaction energy (12) depends both on the geometry of the system, in terms of the parameters D, h, and σ, and on the particular dispersion energies in terms of constants k_1, k_2, and k_3. Equation (12) allows calculating the total force that acts upon the dye molecule in position h

$$F = -\frac{du}{dh} = -\frac{\pi}{2} \left(\frac{k_1 \rho_1 - k_2 \rho_2}{(D+h)^4} - \frac{k_3 \rho_3 - k_2 \rho_2}{h^4} \right). \tag{13}$$

One may now calculate the maximum thickness of the dye layer adsorbed on the solid. To do this one considers that the force between the already adsorbed dye film and a new dye molecule in the solvent placed in contact (or very close) to that film (that is $h = \sigma$) should be zero ($F(\sigma) = 0$), Fig.5.

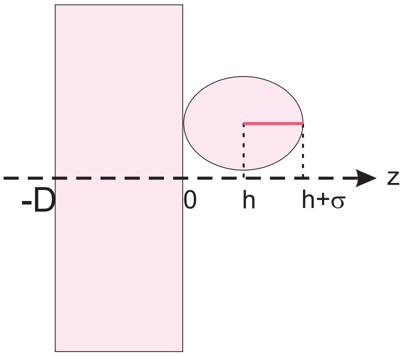


Fig. 5 A dye molecule close to the dye absorbed film.

$$F(\sigma) = -\frac{\pi}{2}\left(\frac{\rho_1 k_1 - \rho_2 k_2}{(D+\sigma)^4} - \frac{\rho_3 k_3 - \rho_2 k_2}{\sigma^4}\right)$$

$$F(\sigma) = 0 \quad \Rightarrow \quad \frac{\rho_1 k_1 - \rho_2 k_2}{(D+\sigma)^4} = \frac{\rho_3 k_3 - \rho_2 k_2}{\sigma^4} \quad \Rightarrow \frac{\sigma + D}{\sigma} = \left(\frac{\rho_1 k_1 - \rho_2 k_2}{\rho_3 k_3 - \rho_2 k_2}\right)^{\frac{1}{4}} \qquad (14)$$

$$\frac{D}{\sigma} = \left(\frac{\rho_1 k_1 - \rho_2 k_2}{\rho_3 k_3 - \rho_2 k_2}\right)^{\frac{1}{4}} - 1 \qquad \Rightarrow \quad D^* = \sigma\left[\left(\frac{\rho_1 k_1 - \rho_2 k_2}{\rho_3 k_3 - \rho_2 k_2}\right)^{\frac{1}{4}} - 1\right]$$

D* is the critical (limit) thickness of the adsorbed dye layer and it depends both on the interaction parameters and the closest approach distance between two dye molecules.

Taken into account the conventional Hamaker constants A_{ij} for medium *i* interacting with medium *j*, defined as [13] $A_{ij} = \pi^2 k_i \rho_i \rho_j$, $i, j = 1,2,3$, usually the following expression is true $A_{ij} = \sqrt{A_{ii}}\sqrt{A_{jj}}$ (where A_{ii} represents the Hamaker constant describing the interaction between two identical media), equation 14 becomes

$$D^* = \sigma\left[\left(\frac{\frac{A_{21}}{\rho_2} - \frac{A_{22}}{\rho_2}}{\frac{A_{23}}{\rho_2} - \frac{A_{22}}{\rho_2}}\right)^{\frac{1}{4}} - 1\right] = \sigma\left[\left(\frac{\sqrt{A_{11}} - \sqrt{A_{22}}}{\sqrt{A_{33}} - \sqrt{A_{22}}}\right)^{\frac{1}{4}} - 1\right] \qquad (15)$$

3. Conclusions

The coverage of a porous TiO$_2$ substrate with adsorbed dye molecules is analyzed. When the solid substrate is immersed in a dye solution, a thin film of adsorbed dye molecules is created due to the attractive force between a dye molecule in the solvent and the atoms of the TiO$_2$ layer. Using the van der Waals interaction potential, the total interaction energy between the media in contact is evaluated. The maximum value of the thickness of the dye layer, D^*, depending on the parameters characterizing the interactions and also on the closest approach distance between two dye molecules is reported. For any dye species it is worth finding a proper solvent such as $D^* \cong \sigma$. An adsorbed monolayer dye provides the maximum efficiency of a DSSC.

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