Research Article

Equilibrium and Kinetic Aspects in the Sensitization of Monolayer Transparent TiO$_2$ Thin Films with Porphyrin Dyes for DSSC Applications

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Free base, Cu(II) and Zn(II) complexes of the 2,7,12,17-tetrapropionic acid of 3,8,13,18-tetramethyl-21H,23H porphyrin (CPI) in solution and bounded to transparent monolayer TiO$_2$ nanoparticle films were studied to determine their adsorption on TiO$_2$ surface, to measure the adsorption kinetics and isotherms, and to use the results obtained to optimize the preparation of DSSC photovoltaic cells. Adsorption studies were carried out on monolayer transparent TiO$_2$ films of a known thickness. Langmuir and Freundlich adsorption constants of CPI-dyes on TiO$_2$ monolayer surface have been calculated as a function of the equilibrium concentrations in the solutions. The amount of these adsorbed dyes showed the accordance with Langmuir isotherm. Kinetic data on the adsorption of dyes showed significantly better fits to pseudo-first-order model and the evaluated rate constants linearly increased with the grow of initial dye concentrations. The stoichiometry of the adsorption of CPI-dyes into TiO$_2$ and the influence of presence of coadsorbent (chenodeoxycholic acid) have been established. The DSSC obtained in the similar conditions showed that the best efficiency can be obtained in the absence of coadsorbent with short and established immersion times.

1. Introduction

TiO$_2$ is a stable, semiconductor with large band gap well known for its considerable applications in dye-sensitized solar cell (DSSC) systems [1, 2] and, for this, several preparation methods have been performed [3–6]. TiO$_2$ nanoparticles layer, together with the dye-sensitizer loaded on its surface, is one of the most important parts of the DSSC structure and, therefore, the optimization of these parameters can enhance the DSSC efficiency.

In the search of new dyes with high extinction coefficient and high DSSC performances, new ruthenium dyes [7], porphyrin dyes [8], and other metal-free dyes [9, 10] are synthesized.

Porphyrins are particularly interesting as photosensitizers for DSSC for the absorption in the 400–450 nm region of Soret band and in the 500–700 nm region of Q-bands and also for the appropriate LUMO and HOMO energy levels; this makes them promising candidates as substitutes for ruthenium dyes in DSSC applications [11].

The increase in the use of porphyrin dyes as sensitizers in DSSC has been very important to clarify the role of natural porphyrins as light harvesting in the photosynthesis; the imitation of this process has been obtained using chlorophyll derivatives as dye sensitizers for nano-TiO$_2$ films [12, 13], showing also the importance of free carboxylic groups for the anchoring on the TiO$_2$ surface [12, 14, 15]. Numerous paper reports have been published on porphyrin dyes as sensitizer for DSSC [5, 16–21].

Cu(II) and Zn(II) complexes of coproporphyrin-I (2,7,12,17-tetrapropionic acid of 3,8,13,18-tetramethyl-21H,23H porphyrin or CPI) have been synthesized in our laboratory and tested as sensitizers in DSSC [22] but mechanism and kinetic in the adsorption of these new porphyrin dyes on TiO$_2$ surface are not clear.

Only few studies, however, focused on kinetics and equilibrium studies on dyes sensitization [23–25]. The aim of this paper was to understand the adsorption mechanism of CPI-dyes on TiO$_2$, also with the use of coadsorbent, to find a suitable equilibrium isotherm and kinetic model useful to...
establish the best operating conditions for the optimization of the DSSC performances. An analytical study of adsorption equilibrium and kinetic control of dyes adsorption is first presented. Successively, the optical properties of CPI-dyes TiO₂ composite thin films are investigated with the purpose of ascertaining the monolayer coverage. Finally, the results obtained are used to optimize the preparation of the photovoltaic cells.

2. Experimental

2.1. Materials. All chemicals (Sigma-Aldrich) were of analytical grade and used without further purification. All the CPI (Figure 1) solutions were prepared into anhydrous ethanol. Copper and zinc CPI complexes (CPICu and CPIZn), synthetized in our laboratory [22], are dissolved with ethanol and 10% DMSO, respectively. Solutions of chenodeoxycholic acid (4 × 10⁻² M) were prepared in ethanol and in ethanol with 10% DMSO and used after dilution from 5 to 20 mM.

2.2. Transparent TiO₂ Films Fabrication. Transparent TiO₂ screen-printed monolayer films used in this study were prepared, from Laboratory for Photonics and Interfaces of Ecole Polytechnique Federale of Lausanne, printing 2.7 μm thick film of 20 nm TiO₂ nanoparticles on the conducting glass electrode (fluorine doped SnO₂ (FTO)) and coating with a second layer of 5 mm thick, composed of 400 nm sized light-scattering anatase particles (CCI, Japan). TiO₂ nanoparticles and paste were prepared as described elsewhere [26]. The porosity for the 20 nm TiO₂ transparent layer, evaluated with BET measurements, was 59% (Monosorb, USA).

2.3. Optical Properties of the CPI-Dyes/TiO₂ Films. All the CPI-dyes/TiO₂ transparent films were sintered at 400° C, cooled to 24° C, immersed every 2 minutes in each dye solutions, washed for remove the dye molecules excess, and, at the end, dried with nitrogen. The UV-visible adsorption of dye/TiO₂ films was recorded on a Hewlett-Packard 8452A diode array spectrophotometer; the absorbance, to remove the interference, was monitored after subtracting TiO₂ film spectrum.

UV-vis absorption intensities of dyes were compared with the data of a calibration curve obtained from different reference solutions after adsorption on TiO₂ films; the content of adsorbed dyes was indicated as surface concentration of dyes (S) and was calculated as reference [23].

2.4. Device Fabrication. The sintered TiO₂ electrodes were immersed for established time in the respective dye solutions, dried by blowing nitrogen, and then assembled with a thermal platinitized FTO/glass counter electrode. The working and counter electrodes, separated by a 25 mm thick hot melt ring (Surlyn, DuPont), were sealed by heating; in the internal space 2960 electrolyte [27] was added with a vacuum pump and a Surlyn sheet covered with a thin glass has been used for sealing the hole.

2.5. Photovoltaic Characterization. To characterize the solar cells, a 450 W xenon light source (Oriel, USA) was used.

Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) was used to match the spectral output of the lamp in the region of 350–750 nm so as to reduce the mismatch between the simulated and true solar spectra to less than 2%. The current-voltage characteristics of the cell under these conditions were obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). To control the incident photon-to-current conversion efficiency (IPCE) measurement a similar data acquisition system was used. Under computer control, light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell under test. The devices were masked to attain an illuminated active area of 0.16 cm².

3. Results and Discussion

3.1. UV-Vis Absorption Spectra of CPI-Dyes/TiO₂ Transparent Films. Figure 2 shows the UV-vis spectra of CPI, CPIZn, and CPICu molecules adsorbed into the films and demonstrates the effective dyes adsorption into the TiO₂ films. All the spectra show the typical strong Soret band of porphyrin molecules (region 400–450 nm) and weak Q bands (region 500–650 nm) that are not changed with respect to solution spectra proving that, in this process, the adsorbed molecules have not modified their structural properties.

3.2. Equilibrium of CPI-Dyes Adsorption. For a good knowledge of adsorption mechanism, necessary for the optimization of the design of an adsorption system, it is important to correlate equilibrium data with theoretical and empirical equations.
To evaluate how the dyes concentration in the original solution influences the adsorption capacity of TiO$_2$ films, different concentration samples have been used. Figure 3 shows the growth of surface concentration of CPI in the different TiO$_2$ films increasing CPI solution concentrations. The adsorption is already high for small dye concentrations and increases to obtain a high value when the solution concentration is about 3.04 $\times$ 10$^{-4}$ M; when the solutions are more concentrated, dye saturation of the film occurs. Similar behaviour has been obtained for Cu and Zn CPI-dyes.

To establish as the dye concentration influence the adsorption process, the equilibrium data has been analyzed by Freundlich (1) and Langmuir (2) isotherms [28, 29]:

$$Q_e = K_F C_e^{1/n}$$  \hspace{1cm} (1)

$$Q_e = \left(\frac{K_L C_e}{1 + a_L C_e}\right)$$  \hspace{1cm} (2)

where $C_e$ (M) is the concentration of the dye solution, $Q_e$ is the amount of dye adsorbed on TiO$_2$ at equilibrium, $K_F$ is the Freundlich constant that represents the adsorption capacity, 1/n is the adsorption intensities, $K_L$ and $a_L$ are the Langmuir constants, and the ratio $K_L / a_L$ gives the theoretical saturation capacity of the TiO$_2$ monolayer, $Q_0$. The linear forms of the two equations can be, respectively, written as follows:

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e$$

$$\frac{Q_e}{C_e} = \left(\frac{1}{K_L}\right) + \left(\frac{a_L}{K_L}\right) C_e.$$  \hspace{1cm} (3)

The linearized isotherm plots were used to calculate the adsorption isotherm constants and the results were summarized in Table I that shows the adsorption data fitting to the Langmuir and Freundlich isotherm models.

The correlation coefficients ($R^2$) for the Langmuir isotherm are highest in comparison to the values obtained for the Freundlich ($R^2_F$) isotherms, indicating that, in the studied concentration range, a Langmuir adsorption relation provides a good description of the CPI-dyes/TiO$_2$ interaction during the adsorption process. As example the plot of $C_e/Q_e$ versus $C_e$ is shown in insert of Figure 3 for CPI adsorption, and the other CPI-dyes show similar behaviour.

According to the Langmuir model, it may be deduced that, in this adsorption process, all dye molecules incorporated into the film have similar adsorption energy, the number of adsorption sites is limited, and the maximum adsorption corresponds to a saturated one layer of dye molecules on the adsorbent TiO$_2$ surface that cannot contribute to an additional incorporation of other molecules.

Interesting to note that, using CPI, when its concentration is greater than 3.04 $\times$ 10$^{-4}$ M, the autoadsorption of dye occurred on TiO$_2$ surface, for probable dye aggregation. In fact, poorly resolved spectrum in the Soret band has been obtained while the absorbance profile in the Q band show typical spectrum of CPI aggregates [22] as reported in Figure 4. Similar behaviour is not obtained for the other CPI-dyes because, for the influence of central metal ion in the complexes, the aggregation of these may occur only at highest concentration.

### 3.3. Kinetics of CPI-Dyes Adsorption

The adsorption of CPI-dyes molecules into TiO$_2$ films was strictly depending on the immersion time as reported in Figure 5 that shows the spectral change in the time for CPIZn dyes adsorbed into monolayer transparent TiO$_2$ films and the evolution in the

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**Table 1: Langmuir ($L$) and Freundlich ($F$) CPI-dyes adsorption constants on TiO$_2$ monolayer surface.**

<table>
<thead>
<tr>
<th></th>
<th>CPI</th>
<th>CPI-Zn</th>
<th>CPI-Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_L$</td>
<td>5.051</td>
<td>3.178</td>
<td>3.037</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>4.90 $\times$ 10$^{-5}$</td>
<td>5.03 $\times$ 10$^{-5}$</td>
<td>6.50 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$a_L$</td>
<td>1.03 $\times$ 10$^5$</td>
<td>6.31 $\times$ 10$^4$</td>
<td>4.67 $\times$ 10$^4$</td>
</tr>
<tr>
<td>$R_L^2$</td>
<td>0.998</td>
<td>0.999</td>
<td>0.998</td>
</tr>
<tr>
<td>$K_F$</td>
<td>7.005</td>
<td>2.323</td>
<td>1.732</td>
</tr>
<tr>
<td>$R_F^2$</td>
<td>0.965</td>
<td>0.805</td>
<td>0.825</td>
</tr>
</tbody>
</table>

---

**Figure 2:** UV-vis spectra and in insert Q-bands magnification for CPI, CPI-Cu, and CPIZn incorporated into the TiO$_2$ films.

**Figure 3:** Growth of surface CPI concentration in the different TiO$_2$ films increasing CPI solution concentrations from 6.08 $\times$ 10$^{-5}$ to 3.04 $\times$ 10$^{-4}$ M; in insert, plot of $C_e/Q_e$ versus $C_e$ according to the Langmuir model.

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time of the surface concentrations of dyes $q_t$ at different solution concentrations of dyes.

The curves obtained at higher dyes concentration show two zones: in the first, the amount of adsorbed molecules grows rapidly while in the second a slowdown of the process occurs because the saturation approaches; all the results showed that the absorption rates depended on initial dye concentrations.

For a correct interpretation of the absorption kinetics, the experimental points were compared with different adsorption kinetic models and the best fit has been observed with a pseudo-first-order model that is a procedure frequently used for the adsorption of a solute from solution [30] and can be expressed by:

$$q_t = q_e \left[1 - \exp(-k_1t)\right]$$  \hspace{1cm} (4)

where $q_t$ is the amount of dye adsorbed at time $t$, $q_e$ is equilibrium solid phase concentration, and $k_1$ is first-order rate constant for adsorption. The linear form is given as follows:

$$\ln\left[\frac{q_e - q_t}{q_e}\right] = -k_1t.$$  \hspace{1cm} (5)

Plotting the first term of (5) versus $t$, good straight lines are obtained and the values of $k_1$ can be deduced (Tables 2, 3, and 4). In the insert of Figure 6 a comparison of calculated and measured results for $8.96 \times 10^{-5}$ M of CPI-dyes, over the entire range of time studied, is reported as an example, showing a good fit to the model; the results indicate therefore that the pseudo-first-order equation provides the best correlation for the these adsorption processes.

However, only for CPI, at concentration of $3.04 \times 10^{-4}$ M, the adsorption took place in two stages (Figure 7) that followed first-order kinetics with respect to CPI concentrations: in the first stage quickly adsorption of CPI occurred while in the slower second step an autoadsorption of CPI was observed.

In Table 2 are reported the values of respective kinetic constants that demonstrate that the monolayer adsorption is about six time faster with respect to layer on layer CPI adsorption. This result can be explained by the adsorption/aggregation competition between CPI molecules and...
Table 2: Kinetic constants for adsorption of different CPI concentrations on TiO$_2$.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>$k_1$ (mol$^{-1}$min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6.08 \times 10^{-6}$</td>
<td>$3.54 \times 10^{-3}$</td>
</tr>
<tr>
<td>$1.23 \times 10^{-5}$</td>
<td>$1.02 \times 10^{-2}$</td>
</tr>
<tr>
<td>$2.21 \times 10^{-5}$</td>
<td>$1.34 \times 10^{-2}$</td>
</tr>
<tr>
<td>$8.96 \times 10^{-5}$</td>
<td>$1.01 \times 10^{-1}$</td>
</tr>
<tr>
<td>$3.04 \times 10^{-4}$</td>
<td>$19.31 \times 10^{-1}$*</td>
</tr>
<tr>
<td>$3.04 \times 10^{-4}$</td>
<td>$3.21 \times 10^{-1}$*</td>
</tr>
</tbody>
</table>

$k_1 = 1188.9 \times C_{CPI} - 0.0066$  $R^2 = 0.992$

*first step kinetic; second step kinetic.

Table 3: Kinetic constants for adsorption of different CPI$_2$Zn concentrations on TiO$_2$.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>$k_1$ (mol$^{-1}$min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.24 \times 10^{-6}$</td>
<td>$3.41 \times 10^{-3}$</td>
</tr>
<tr>
<td>$1.22 \times 10^{-5}$</td>
<td>$1.48 \times 10^{-2}$</td>
</tr>
<tr>
<td>$2.44 \times 10^{-5}$</td>
<td>$3.73 \times 10^{-2}$</td>
</tr>
<tr>
<td>$3.16 \times 10^{-4}$</td>
<td>$64.67 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

$k_1 = 2.08 \times 10^{3}C_{CPIZn} - 9.68 \times 10^{-1}$  $R^2 = 0.999$

3.4. Effect of Chenodeoxycholic Acid on the Dyes Adsorption. The effect of aggregation on the TiO$_2$ surface must be carefully considered and clarified for improving the cell performance of porphyrin-based DSSC [31]; the porphyrin molecules aggregation is the result of π-stacking and is a serious problem because the aggregates do not generate photocurrent [31]. The addition of a coadsorbent onto the dye solutions, during the dye-coating process, can be useful for the suppression of dye aggregation on the TiO$_2$ surface. Chenodeoxycholic acid (CDCA) is the most popular coadsorbent that, adsorbing on the TiO$_2$ surface thanks to their carboxyl and hydroxyl groups, restricting dye aggregation in DSSC assembly [18, 32].

For evaluating the effect of CDCA concentrations on the adsorption of CPI-dyes on TiO$_2$ surfaces, solutions of dyes with different CDCA concentrations have been used. In Figure 8 are reported, as example, the adsorption kinetics for CPI varying the CDCA concentrations, which clearly demonstrate that the adsorption of dyes decreased with an competitive effect on the adsorption that depended on CDCA concentrations. Also the kinetics of these process changed confirming the competition of CDCA in the adsorption of CPI-dyes for the suppression of the adsorption of CPI-dye molecules on the TiO$_2$ surface.

3.5. Stoichiometry of the Adsorption Process and Photovoltaic Measurements. The evaluation of the number of CPI-dye molecules adsorbed on the TiO$_2$ surface permits calculating the stoichiometry of the adsorption process. The effective adsorption surface of TiO$_2$ monolayer has been calculated from the TiO$_2$ roughness [33], porosity, and exposed surface parameters. Therefore, assuming full coverage of this, it is possible to estimate the number of CPI-dye molecules which...
could be adsorbed. Knowing in fact the effective surface area of CPI-dye molecules that is approximately $1.31 \times 10^{-14} \text{ cm}^2$, it is possible to calculate the theoretical degree of covering (DC)$_T$ that can be compared with that experimental (DC)$_E$ as reported in Table 5.

From the ratio between theoretical (DC)$_T$ and experimental (DC)$_E$ values, obtained after immersion of 30 min for CPIZn and 60 min for CPI and CPICu with different CDCA concentrations, it may be deduced that the CPI-dyes form a single layer on the TiO$_2$ surface, in which the increase of CDCA concentration causes a competition with the dyes to the active sites on the semiconductor and consequently less dye molecules are adsorbed.

From the results obtained, since the amount of dye adsorbed on the TiO$_2$ film changed with time and with CDCA concentrations, it was also interesting to investigate the change of photovoltaic properties with adsorption time and coadsorbent.

Figure 9 shows the results of photocurrent-voltage curves for different experimental conditions of CPIZn and CPICu dye solutions, respectively, and the relevant photovoltaic parameters are listed in Table 6.

It is very important to consider that in the presence of CDCA 2 mM the Voc values increased but, only at long adsorption times, this is translatable in an increase in efficiency.
Table 6: Effects of adsorption time and CDCA on the short-circuit photocurrent density (Jsc) open-circuit voltage, fill factor (FF), and overall conversion efficiency (η) of dye-sensitized solar cells based on CPICu and CPIZn (0.3 mM) with 2.7 μm thick monolayer TiO2 film and using Z960 as electrolyte under an illumination of the AM 1.5G full sunlight intensity.

<table>
<thead>
<tr>
<th>Dye</th>
<th>CDCA</th>
<th>Adsorption time (min)</th>
<th>Jsc (mA/cm²)</th>
<th>Module $U_{oc}$ (mV)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CPIZn</td>
<td>—</td>
<td>1440</td>
<td>3.62</td>
<td>549.12</td>
<td>73.54</td>
<td>1.48</td>
</tr>
<tr>
<td>CPIZn</td>
<td>—</td>
<td>30</td>
<td>4.38</td>
<td>579.10</td>
<td>70.36</td>
<td>1.86</td>
</tr>
<tr>
<td>CPIZn</td>
<td>2 mM</td>
<td>1440</td>
<td>4.23</td>
<td>562.48</td>
<td>69.88</td>
<td>1.80</td>
</tr>
<tr>
<td>CPIZn</td>
<td>2 mM</td>
<td>30</td>
<td>3.98</td>
<td>590.31</td>
<td>70.96</td>
<td>1.77</td>
</tr>
<tr>
<td>(b) CPICu</td>
<td>—</td>
<td>1440</td>
<td>4.66</td>
<td>626.64</td>
<td>71.85</td>
<td>2.10</td>
</tr>
<tr>
<td>CPICu</td>
<td>—</td>
<td>60</td>
<td>4.65</td>
<td>668.20</td>
<td>70.36</td>
<td>2.20</td>
</tr>
<tr>
<td>CPICu</td>
<td>2 mM</td>
<td>1440</td>
<td>4.70</td>
<td>650.19</td>
<td>69.88</td>
<td>2.14</td>
</tr>
<tr>
<td>(c) CPICu</td>
<td>2 mM</td>
<td>60</td>
<td>3.89</td>
<td>686.50</td>
<td>70.94</td>
<td>1.89</td>
</tr>
</tbody>
</table>

In fact, as it can be seen in Table 6, for the CPIZn dye, in the presence of CDCA 2 mM and with the adsorption time of 1440 min, the efficiency is greater than that in absence of CDCA; on the contrary when the adsorption time is of 30 min, in the presence of CDCA, the efficiency is lower with respect to that without CDCA; similar results were obtained with CPICu.

However, in the absence of CDCA, monolayer coverage is expected to be formed in 30 min for CPIZn and 60 min for CPICu, while multilayer (due to dye aggregation) is expected only after these times. Because the dye aggregates have been known to be inactive for electron injection and shield the dye molecules in direct contact with TiO2 from absorbing light, it is thus expected that, in the absence of CDCA, long adsorption time exhibits lower photocurrent in spite of higher dye loading.

The best efficiencies are obtained at 30 min adsorption from CPIZn solution and at 60 min adsorption from CPICu, in the absence of CDCA, condition in which a single layer of the dyes is obtained as verified from the stoichiometry of adsorption process (see Table 5).

So, for both CPIZn and CPICu the use of CDCA is negative for short immersion times because, thank of its competition with CPI-dyes, the dye coverage on TiO2 surface decrease, while is positive only with long immersion times probably because it permits the evolution of adsorption process with reduction of dye aggregation on the TiO2 surface. For these results the adsorption mechanisms of CPI-dyes in the presence and in the absence of CDCA can be explained as shown in Figure 10.

4. Conclusions

For the best manufacture of DSSC devices, optimum objectives are represented by very rapid and complete adsorption of single layer of dye on the semiconductor surface.

In this study we have described that the CPI-dyes concentration and adsorption times affected the dyes adsorption...
on TiO$_2$ monolayer surfaces and consequently the DSSC performances.

The analytical study, with the equilibrium and kinetic data presented for adsorption of CPI-dyes onto TiO$_2$ monolayer surfaces, also in the presence of CDCA as coadsorbent, has allowed us to establish the best experimental conditions for the adsorption of these dyes and has demonstrated that the CPI-dyes, according to the Langmuir model and with pseudo-first-order kinetics, are adsorbed effectively on the TiO$_2$ monolayer without chemical changes. A systematic study of kinetic and equilibrium has been proposed demonstrating that the suppression of the dyes aggregation permits the optimization of selective adsorption of one layer of dyes molecules to stoichiometric ratios indicating a powerful strategy, which can be applied to other dyes, for improving performances in DSSC.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this article.

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