Redox Properties of Cobalt Tetraphenyl Porphyrin Adsorbed on Semi-Conductor Oxides Studied by Photoacoustic Spectroscopy

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Photoacoustic spectroscopy has allowed to show that physisorbed CoIII TPP is ground state monooxidized into (CoIII TPP)+ when adsorbed on Nb2O5, TiO2, SrTiO3, ZnO, SnO2. A double oxidation is observed when the porphyrin is adsorbed on WO3. On the contrary when it is adsorbed on ZrO2 and SiO2, oxidation only occurs if the porphyrin has been driven by irradiation in its excited state. It remains in the reduced form when adsorbed on Ta2O5. This behavior has been correlated with the band positions of these various oxides and has allowed to roughly position the oxidation potential of CoTPP in adsorbed state ~0.8 V higher than in solution (0.5 V/SCE or 5.3 V/vacuum) that is 4.5 V/vacuum.

INTRODUCTION

Photocatalytic effects of semi conductors have been under investigation for a long time because of their potential application to direct conversion of solar energy into chemical energy. The irradiation of the semi conductor with an energy higher than the band-gap is accompanied by the promotion of an electron from the valence band to the conduction band. Either the hole left in the valence band or the electron may be used for further chemical reaction or current generation. One of the problems of the photo electrochemical cells for solar energy storage is the choice of the semi conductor. When narrow band gap semi conductors which are good absorbers of solar
spectrum are used such as CdS, a strong anodic decomposition is observed which degrades the semiconductor. On the other hand, the inconvenience of the wide band gap semi conductors such as TiO$_2$, SrTiO$_3$ which are stable against photo anodic decomposition is that they are poor absorbers of the solar spectrum. In order to remedy this situation it has been tempted to sensitize the semiconductor. The sensitization may be realized by introduction of impurity dopants in the semi conductor lattice such as Cr$^{3+}$ ions in titanium dioxide$^{4,5}$ or by chemical derivatization of the surface of the semi conductor.$^6$ Another possibility consists in the adsorption of visible light absorbing organic material at the surface of the semi conductor. Most of the compounds which have been used in such an aim are dyes.$^7$ It has been shown that they are oxidized and inject an electron into the semi conductor after being excited by absorption of light.$^8$ The dynamics of such sensitization process has been studied in the case of rose bengal on ZnO.$^9$ Further studies have made evident that the quantum efficiency for the photoinjection of electrons, in the case of rose bengal on TiO$_2$ was independent of the pH and of the dye surface concentration.$^{10}$

Porphyrians are other organic compounds which are good candidates for sensitization of semi conductors. They strongly absorb the visible light and are able to undergo a wide variety of electron exchanges.$^{11}$ They have been tentatively used directly for water photooxidation$^{12}$ and for photoinduced redox reactions in aqueous micelles.$^{13}$ Their behavior when being adsorbed on electrodes has also been studied. When being deposited on a photo inactive electrode such as platinium or carbon, they may induce oxidation properties of the electrode that normally undergoes reduction when being illuminated. In the case of an aluminum electrode it has been shown that the system is photoactive and best described by a metal–insulator–semi conductor Schottky barrier consisting of Al/Al$_2$O$_3$/porphyrin where the porphyrin behaves as a $p$-type semi conductor.$^{14}$ The sensitization of semi conductor electrodes by porphyrins has also been investigated.$^{15,11}$ Photochemical measurements have shown that a $n$-type SnO$_2$ semi conductor electrode acts as a photo cathode when sensitized by a layer of meso-tetraphenyl porphyrin$^{16}$ instead of the usual photo anodic behavior.

However, it is to be noted that the interface porphyrin/electrode has never been studied directly as mostly electrochemical techniques have been used to investigate the sensitized electrode. One of the
reasons for such a lack is the difficulty in applying classical spectroscopic techniques to the investigation of an opaque interface. Photoacoustic spectroscopy is a technique which has been recently developed that can overcome this problem as it allows the direct observation of the absorption spectrum of opaque samples. The sample, contained in a tight cell is irradiated with monochromatic modulated light. The absorbed energy is converted into a heat wave via the radiationless transitions. This heat wave propagates through the sample and the cell gas and transforms into a pressure wave within the cell which is detected with a microphone. The theoretical treatment done by Rosencwaig and Gersh7 shows that the microphone signal always depends upon the thermal properties of the sample and, when not saturated depends also on the optical properties of the sample. Furthermore, by varying the frequency of modulation of the light it is possible to determine these optical properties at various depth of the sample which is quite favorable for the study of an interface. The photoacoustic spectrum is recorded by measuring the microphone signal as a function of the irradiation wavelength. It is truly a radiationless excitation spectrum.

Photoacoustic spectroscopy has been recently applied to photo electrochemical investigations. The change in the absorption spectrum of a ZnO electrode upon electrolysis has been investigated. Sensitization studies have just started: dye oxidation has been observed at fixed wavelength as a function of the applied potential on an SnO2 electrode. Chemical modification of the dye as a function of irradiation has been studied in the case of RhB adsorbed on ZnO which undergoes deethylation.

In this work, we have applied photoacoustic spectroscopy to the investigation of the interface obtained by adsorption of cobalt tetraphenyl porphyrin on various semiconductor oxides and insulators. In order to study the electron exchanges at this interface we have determined the oxidation state of the adsorbed porphyrin by observing its photoacoustic spectrum depending on the substrate and irradiation.

EXPERIMENTAL

Commercial semiconductor oxides provided by Merck have been used. It has been checked that a nitric acid etching had no influence
on the observations. Thus the oxides have been used without any
chemical treatment. Any how, in order to eliminate water and oxygen
effects they have been heated at 130°C during 12 hours, degassed up
to $10^{-5}$ torr and kept under dry nitrogen until used.

The porphyrins have been prepared according to the literature. They have been further purified by thin layer chromatography on
silicic acid Merck 60 and stored in the dark in absence of oxygen.

The adsorption of the porphyrin on the oxides was realized by
allowing a methylene chloride solution of porphyrin to contact the
degassed oxide. A $10^{-4}$ M solution concentration was chosen as being
a good compromise for having a good signal to noise ratio in the
spectra and weak aggregation effects. It was checked that 2 hours
contact were sufficient to allow the adsorption equilibrium to be
reached. The surfonagent solution was then eliminated by filtration,
the oxide was vacuum dried and finally transferred under nitrogen
pressure in the photoacoustic cell. A 20 mg sample is needed for
making a photoacoustic spectrum. Any how, in order to facilitate the
manipulation we have worked with 100 mg oxide and 1 ml $10^{-4}$ M
porphyrin solution. Such an experimental procedure has been adopted
in order to prevent undesirable oxygen and water effects. Indeed we
have observed extra oxidation of the CoTPP when being adsorbed
on Al$_2$O$_3$ in presence of oxygen. We have also observed that the
photoacoustic spectrum of CoTPP adsorbed on ZnO is broadened
and red shifted of as much as 5 nm in presence of water. Any how
we have not studied this effect quantitatively.

We have calculated the surface concentration of the porphyrin. We
have measured the specific surface of the oxides using BET technique
and determined the amount of adsorbed porphyrin by eluting with
chloroform the sample and measuring the optical density of the
elution. Under the assumption that the molecule lies flat on the oxide
one obtains a surface concentration varying from $10^{-2}$ to $10^{-1}$
monolayer depending on the oxide, which tends to demonstrate that
the porphyrin is adsorbed in monomeric form. Indeed we have ob-
served a significant broadening of the spectra when the methylene
chloride solution concentration is raised from $10^{-4}$ M to $10^{-3}$ or
$10^{-2}$ M indicating in such a case the existence of aggregates.

The photoacoustic spectra have been taken in an EDT instrument.
We have checked by measuring the frequency dependence of the
signal that there was no saturation at the frequency of 80 Hz which
has been used for all the spectra. The experimental spectral resolution was 4 nm and it has been checked that it was not a limitation for the observations.

RESULTS

The photoacoustic spectra of the various oxides are represented on Figure 1. They are in agreement with the bands position determined by other methods.24,25,26

The spectral modifications of the porphyrin induced by adsorption are shown on Figure 2 in the case of the free base tetraphenyl porphyrin that undergoes less easy oxidation than CoTPP. The major features are the broadening of the spectrum and the decrease of the intensity ratio of the Soret band relative to the visible ones which is due to interaction with the substrate in the adsorbed state.

![Figure 1: Photoacoustic spectrum of the degassed oxides (when water is present red shifts in the spectra may be observed).](image-url)
When cobalt porphyrin has been adsorbed on an oxide, the observed photoacoustic spectrum is the sum of the porphyrin and of the oxide absorption spectra because of the weak porphyrin surface concentration. It has been checked that an increase in the frequency modulation of the light which allows a more superficial observation of the sample did not eliminate the oxide absorption. When this latter interfered with the porphyrin absorption, deconvolution of the spectra has been done.

In solution, the valency of the cobalt atom in cobalt tetraphenyl porphyrin is II. The optical spectrum, of Co\textsuperscript{II}TPP consists in a Soret band at 415 nm and a broad visible band at 540 nm.\textsuperscript{27} Easy oxidation may occur through valency change of the central metal atom. The (Co\textsuperscript{III}TPP)	extsuperscript{+} has a red shifted optical spectrum with a Soret band at 438 nm and two visible bands at 550 and 590 nm.\textsuperscript{28,29} The second
oxidation step takes place at the ligand and \((\text{Co}^{III}\text{TPP})^{++}\) exhibits a weak absorption spectrum with a broad band around 600 nm.\(^{28}\)

In adsorbed state we have observed that the cobalt porphyrin has the same behavior as in solution: depending on the oxide the three types of spectra which have just been described may be observed which proves that oxidation takes place in the adsorbed state in the same way as it does in solution i.e., via the metal first and then via the ligand. The \(\text{Co}^{II}\text{TPP}\) spectrum is observed when the porphyrin is adsorbed on \(\text{Al}_2\text{O}_3\) and \(\text{Ta}_2\text{O}_5\). It consists in a Soret band at 400 nm and a visible band at 520 nm (Figure 3). We have observed that in both cases when the concentration of the porphyrin solution in contact with the oxide is lowered, the mono-oxidized form of the porphyrin appears \((10^{-5}\, \text{M})\) and becomes preponderant \((10^{-6}\, \text{M})\).

On \(\text{SiO}_2\) and \(\text{ZrO}_2\) substrates, the \(\text{Co}^{II}\text{TPP}\) spectrum is initially observed. However, photo-oxidation occurs as \(\text{Co}^{II}\text{TPP}\) transforms

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**FIGURE 3** Photoacoustic spectrum of cobalt tetraphenyl porphyrin adsorbed on \(\text{Ta}_2\text{O}_5\). \(\text{Co}^{II}\text{TPP}\) spectrum is preponderant at \(10^{-4}\, \text{M}\). As lowering the concentration to \(10^{-6}\, \text{M}\) the \((\text{Co}^{III}\text{TPP})^{+}\) spectrum appears. The indicated concentration is the porphyrin/\(\text{CH}_2\text{Cl}_2\) solution one.
in (Co$^{III}$TPP)$^+$ upon excitation of the porphyrin as made evident on Figure 4. The irradiation has been done by 5 s steps with an XBO 450 W lamp filtered in such a way that only light at higher wavelength that 400 nm could pass.

When the porphyrin is adsorbed on all the other oxides except WO$_3$ that is: SnO$_2$, Nb$_2$O$_5$, TiO$_2$, ZnO, SrTiO$_3$ both type spectra (Co$^{II}$TPP and Co$^{III}$TPP$^+$) are concomitantly observed (Figure 5). In all these cases photo-oxidation is not observed. However, at long irradiation time (60 s) a photodestruction of the cycle occurs as the spectrum vanishes without the apparition of new bands. This photo-chemistry is more efficient on the already oxidized form of the porphyrin.

In the case of WO$_3$ the spectrum vanishes and, after subtracting the absorption of the oxide, one observes a broad and weak band that we have interpreted as due to the absorption of the doubly oxidized form (Co$^{III}$TPP)$^{++}$.

![FIGURE 4](image-url)  
**FIGURE 4** Photoacoustic spectrum of cobalt tetraphenyl porphyrin adsorbed on ZrO$_2$. Evidence for photooxidation: (1) without irradiation (CO$^{II}$TPP), (2) 5 s irradiation, (3) 10 s irradiation (Co$^{III}$TPP)$^+$. 
DISCUSSION

We have tempted to interpret the observations relating the energy levels of the semiconductors with the oxidation potential of the porphyrin. We shall reference them to vacuum level as all observations have been made in absence of electrolyte. A conversion to standard calomel electrode is done by substracting 4.75 V which is the potential of the electrode relative to vacuum.

The bands energies of the oxides are indicated on Figure 6. The positions of the Fermi levels have been obtained by the calculated electronegativities. The positions of the conduction bands are obtained by the electron affinities calculations or flatband potential measurements. The valence bands are positioned from the knowledge of the band gaps.

The oxidation potentials of the cobalt porphyrin measured in 0.1 M $n$-Bu$_4$NBF$_4$/benzonitrile solution and corrected for electrolyte effect are indicated in Ref. 28. The metal oxidation potential is
5.27 V/vacuum (0.52 V/SCE) and the ligand second oxidation potential is at 5.94 V/vacuum (1.19 V/SCE). One has to note that the monooxidation potential lies at lower energy than the conduction band of all the oxides (Figure 6). It is thus difficult to account for different oxidative behaviors when the porphyrin is deposited on the different oxides and furthermore to account for any oxidation of CoTPP which is usually interpreted as isoenergetic electron transfer from the porphyrin to the semi conductor conduction band. Thus we propose, in order to interpret the observations that the oxidation potential of tetraphenyl porphyrin in adsorbed state lies at higher energy than in solution.

We have tentatively positioned the oxidation potential of the porphyrin in the adsorbed state with the following hypotheses:

The porphyrin oxidation potential in adsorbed state does not depend on the oxide which is justified by the fact that we try to make only an evaluation of this potential.

The oxidation potential of the excited porphyrin differs from the ground state one only by the energy difference between the ground state and the first excited singlet state.

Ground state oxidation as well as excited state oxidation occur via an isoenergetic transfer from the porphyrin to the conduction band.
of the semiconductor at the energy of highest density of states in the conduction band that is about 0.8 eV higher than the lower limit.

No band bending will be considered for the interpretation as the observations have been done in absence of electrolyte.

With these hypotheses and considering that CoTPP is photo oxidized when adsorbed on SiO₂ and ZrO₂, we may position the oxidation potential of excited CoTPP at the level of the conduction band of these oxides that is around 2.5 V/vacuum. Taking into account that the energy difference between the ground and the excited state of CoTPP is 2 eV we may position the ground state oxidation potential of CoTPP at 4.5 eV/vacuum which is about 0.8 eV higher than the corresponding potential in solution. Such a value is quite reasonable as it is known that, in solution, changes in solvant polarity induce shifts in the oxidation potential up to 0.5 V. Thus it is not surprising to find such an important change when going from solution to adsorbed state. The ground state oxidation potential evaluated in such a way lies at higher energy than the conduction level of SnO₂, Nb₂O₅, TiO₂, ZnO, SrTiO₃. It is thus understandable that oxidation may take place in the ground state when the porphyrin is adsorbed on those substrates. However it is not complete and is almost inexistant in the case of Ta₂O₅ as the conduction band of this latter lies at slightly higher energy (Figure 6).

It is possible to make an evaluation of the second ground state oxidation potential in the same way; one finds 5.1 V/vacuum, a value which is higher than the lowest level of the conduction band of WO₃ which explains the double oxidation in this case (Figure 6).

The Al₂O₃ conduction band lies at such a high energy (Figure 6) that neither excited state oxidation nor (a fortiori) ground state oxidation of the porphyrin is possible when it is adsorbed on this substrate. The apperition of (Co⁺³TPP)⁺ spectrum when lowering the concentration in the case of Al₂O₃ or Ta₂O₅ may be interpreted in term of imperfect degassing of the powder or presence of lattice impurities creating low lying states that allow oxidation of the porphyrin.

CONCLUSION

Photoacoustic spectroscopy has allowed to directly study the interface adsorbed porphyrin/semiconductor oxide by observation of the porphyrin spectrum. It has shown that:
The redox properties of the cobalt tetraphenyl porphyrin are similar in solution and in adsorbed state.

The oxidation potential of the cobalt porphyrin in adsorbed state is higher than in solution.

However, this technique has only allowed to study the interface in absence of electrolyte. Further work is in progress using beam depletion techniques in order to study the oxidation state of the porphyrin in presence of an electrolyte that is in a more realistic condition for an application of the porphyrin sensitized semi conductor system for energy storage.

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