Evaporated porphyrin films as nitrogen dioxide gas sensors

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Abstract. In this work, metal-free and copper(II) 5,10,15,20-tetrakis(-4-(methyl 2-phenoxyacetate)) porphyrin films were employed as nitrogen dioxide gas sensors. The films were vacuum evaporated and the sensor response was evaluated as changes in the optical absorption spectra, hydrophobic properties and conductivity at different gas concentrations. The morphology of the films obtained with scanning electron and atomic force microscopy before and after gas exposure indicated different interaction mechanisms. For instance, metal-free film exhibited an absorption phenomenon due to gas diffusion towards the bulk film because of the presence of pores at the film interface, while the copper-porphyrin film showed interfacial film degradation. From UV-vis results, differences in the gas content within the film were detected due to the formation of new peaks around 680 nm in agreement with morphological findings. Contact angle results exhibited less hydrophobic films after gas adsorption as a result of changes in the surface roughness. In addition, the conductivity values were not only dependent on the gas concentration but also on the molecular structure. For instance, gas absorption within the metal-free films truncated electron mobility paths decreasing the conductivity response in comparison with the copper system. Finally, the molecular packing arrangement and gas absorption were also investigated by using density functional theory, which provided some insights into the molecular-gas interactions and supported experimental results.

Keywords. Porphyrin; gas sensor; nitrogen dioxide; DFT.

1. Introduction

Recently, organic thin films have been investigated as promising materials to detect harmful volatile toxic compounds. In particular, conjugated macrocycles such as porphyrins have been employed since they exhibit rich redox activity, a characteristic absorption spectra and the ability to transfer charge carriers among other properties. For instance, changes in the absorption spectra of these films after gas absorption have suggested that these systems represent a reliable and economical method for the fabrication of portable gas sensor devices [1,2].

Previous work showed that porphyrin molecules can be easily coordinated with different central metal atoms or ligands to modify the magnitude of the sensing response [3]. For instance, metal-free porphyrin films have been employed to detect CO₂ and nitrogen dioxide (NO₂) toxic gases, while magnesium-modified porphyrin films have been used to detect 2-methyl-2-butanol alcohol [4]. Moreover, copper porphyrins (CuP) have been used as gas sensors, since Cu exhibits different spin states that not only influence the electron transfer, but also the charge distribution when exposed to various volatile compounds [5]. Gu *et al* [5] showed that the CuP-N₂ interaction is the strongest among different compounds, and therefore, exhibits a good binding ability that can increase the detection response.

On the other hand, oxidizing gases such as NO₂ have attracted considerable attention since they are found in the atmosphere with very harmful effects on all life forms. Although previous work suggested that the sensing characteristics of NO₂ by using porphyrins remain active over a long period of time, no evidence has been shown on the effects of the gas on the porphyrin macrocycle, packing molecular arrangement or film integrity.

Over the last few years, some experiments have been carried out to investigate the sensitivity of porphyrins in solution [2], thin films formed by using the Langmuir-Blodgett technique [6–9] and spin-coating [10] to detect volatile compounds. Another aspect to consider is the lack of reproducibility of the sensing response, which can be attributed to the thickness of the films, among others. Unfortunately, little work has been devoted to investigate vacuum evaporated films in spite of producing very robust and homogeneous organic films, which can provide some information regarding the thickness effect on the film integrity and reproducible response.

So, in this work, we employed two newly synthesized metal-free and copper(II) 5,10,15,20-tetrakis(-4-(methyl 2-phenoxyacetate)) porphyrin molecules as thin films to investigate their capacity to detect NO₂ by looking at changes in the absorption spectra, morphology, contact angle and their *in-situ* conductivity. In addition, density functional

theory (DFT) computer simulations were also performed to understand the experimental results and provide some insights regarding the absorption mechanisms for gas detection.

2. Experimental

Metal-free (M1) and copper(II) 5,10,15,20-tetrakis(4-methyl 2-phenoxyacetate)) (CuM1) porphyrin molecules were synthesized and used without further purification [11]. The films were deposited onto quartz and indium tin oxide (ITO) substrates for the optical and electrical characterization, respectively. The physical vapour deposition technique was employed by using the VCM600 system from Norm Electronics Ltd working at 10^{-6} mbar. Spectroscopic measurements of the films were carried out with the UV-vis Bluewave miniature StellarNet spectrometer before and after gas absorption in the 400–1000 nm wavelength interval. The morphology of the films was investigated with a field emission scanning electron microscope JSM-7800F from JEOL using the gentle beam mode to avoid damage to the films. Furthermore, atomic force microscopy (AFM) images of the films interface were acquired with a JEOL JSPM-4210 microscope in the tapping mode. Surface characterization was performed

before and after gas exposure to investigate morphological changes. The presence of the gas was also established with the energy dispersive spectroscopy technique by using elemental analysis with an Aztec energy standard microanalysis system. Conductive measurements of the films were acquired in a homemade device inside a gas chamber to investigate the *in-situ* conductivity of the films during exposure. For this purpose, a dual tip setup connected to a power supply (Keithley 2400 SourceMeter) was employed. Prior to the gas injection, to establish a reference signal, a 1 mA current was injected to the films and the voltage variation during gas exposure was obtained as a function of time. The NO_2 gas was produced by the chemical reaction of highly pure (99.9%) copper wire and reagent grade concentrated nitric acid 70% from Sigma-Aldrich at different gas concentrations (20, 40 and 80 ppm) assuming a 100% conversion. The reaction container was connected to the conductive measurement chamber of 0.64 l volume. The gas was introduced at a constant flow rate to maintain the same experimental conditions in all cases. All experiments were carried out at room temperature.

On the other hand, DFT calculations were performed to investigate the molecular interactions between porphyrin and gas molecules by using the hybrid B3LYP/6-31(d,p) basis set, since it has provided good agreement with experimental

Figure 1. SEM images of (a) bare ITO, (b) M1 film as deposited, (c) M1 film after 40 ppm and (d) M1 film after 80 ppm. Image sizes are (a) 25,000 $\times$ and (b), (c) and (d) 10,000 $\times$.

results on porphyrin systems [12]. For this study, all systems were fully optimized and the calculations were performed with the Gaussian 09 program package.

For the simulations, two different configurations for each porphyrin system were considered: (a) the interaction of one NO_2 group at different positions on the porphyrin molecules, i.e., NO_2 –porphyrin and (b) the interaction of two porphyrin molecules (dimer) and one NO_2 group, i.e., porphyrin– NO_2 –porphyrin. In the latter case, the optimized porphyrin self-assembled system was employed to provide not only relevant information regarding the possible packing of the molecules within the film, but also the effect of the NO_2 molecule on this arrangement, since it has been observed that dimer calculations on porphyrin systems are sufficient to model large-scale aggregations [13].

3. Results

3.1 Experimental

After evaporation, the average thicknesses of the M1 and CuM1 films were 150 nm. Figures 1 and 2 show the scanning electron microscopy (SEM) images of the metal-free M1 and

CuM1 porphyrin films before and after gas absorption. Panel a exhibits the ITO surface prior to the film deposition, while panel b shows the as-deposited porphyrin films, respectively, which exhibit uniform deposits with irregular aggregates on the film surface suggesting an island growth mechanism on top of the fully formed films. Panel c and d shows the surface after being exposed to NO_2 at concentrations of 40 and 80 ppm, respectively. From panels c and d important differences can be observed. In the metal-free film, the gas interaction produced pores of diameters between 20 and 700 nm, while the copper porphyrin interface showed a granular aspect with irregular features between 50 and 800 nm. In both cases, the density of pores/grains increased as the gas concentration augmented.

High-magnification 3-D images (figures 3 and 4) and the surface roughness were obtained with an AFM. Panel a corresponds to the ITO surface, while panel b corresponds to the as-deposited M1 and CuM1 films prior to gas exposure. Panel c and d shows the films after 40 and 80 ppm, respectively. The surface of the metal-free films show the formation of pores with diameters between 50 and 600 nm, while the copper film exhibit grains in agreement with SEM results. The roughness values for images in

Figure 2. SEM images of (a) bare ITO, (b) CuM1 film as deposited, (c) CuM1 film after 40 ppm and (d) CuM1 film after 80 ppm. Image sizes are (a) 25,000 $\times$ and (b), (c) and (d) 10,000 $\times$.

Figure 3. AFM images of (a) bare ITO, (b) M1 film as deposited, film after (c) 40 ppm and (d) 80 ppm of gas exposure. All images are $10\ \mu\text{m} \times 10\ \mu\text{m}$.

figure 3 are (a) 6.2, (b) 1.52, (c) 26.59 and (d) 18.56 nm, and in figure 4 are (a) 6.22, (b) 2.22, (c) 31.68 and (d) 26.31 nm, respectively.

From SEM and AFM results, it is clear that irreversible damage to the films is observed, as suggested by other groups. What is interesting from these images, is that the gas attack mechanism on the films is not the same, and therefore, the influence of the central metal atom is dominant in this process.

The optical absorption spectra of the films before and after NO_2 gas exposure for the (a) metal-free and (b) copper porphyrin films are shown in figure 5. In figure 5a, the solid line that represents the film before gas exposure show the typical spectra of a porphyrin system with the Soret (457 nm) and four Q bands (524, 559, 599 and 655 nm). After gas absorption, the Soret peak exhibits an important reduction as well as a 25 nm bathochromic shift for all gas concentrations to 482 nm, which can be attributed to important changes in ring conjugation due to oxidation effects. In addition, other bands at 541, 581, 611 (small shoulder) and 678 nm increased their magnitude as the gas concentration augmented.

The spectra of the copper porphyrin film before gas exposure, as shown in figure 5b, show the Soret peak at 450 nm and two Q peaks at 547 and 580 nm in agreement with other Cu porphyrin compounds [14]. After NO_2 gas exposure, a small redshift and the broadening of the Soret band at 455 nm occurred. In addition, the Q bands disappeared and one small shoulder and peak appear at 550 and 686 nm, respectively. One aspect of this result is related to the intensity of the peak at different gas concentrations. For instance, the Soret peak decreased its intensity as the gas concentration increased, while the new peaks showed the opposite trend similar to the metal-free system. Another important feature of these plots is that the position of the new Soret and other peaks is nearly the same regardless of the gas concentration for each compound.

By using the Tauc model, the optical band gap for the M1 film decreased from 2.60 eV for the as-deposited film to 2.40 eV for all concentrations after gas exposure. On the other hand, a band gap of 2.70 eV was obtained for the CuM1 as-deposited film, while a 2.48 eV was obtained for all gas concentrations. In both cases, a small decrease in the

Figure 4. AFM images of (a) bare ITO, (b) CuM1 film as deposited, film after (c) 40 ppm and (d) 80 ppm of gas exposure. All images are $10\ \mu\text{m} \times 10\ \mu\text{m}$.

optical band gap was observed after gas exposure. Similar results have been reported by Richardson *et al* [9] when using Langmuir–Blodgett metal-free porphyrin films.

The conductivity response of the metal-free and copper porphyrin films for various NO_2 concentrations is shown in figure 6. From these plots, it is clear that the voltage increases as the gas concentration augments, in both cases. For the 80 ppm gas exposure, the largest saturation voltage for M1 was 0.23 V, while for the same gas concentration the maximum voltage for CuM1 was 0.42 V, indicating a better conductive response in the latter case.

Contact angle measurements of the films before and after gas exposure are shown in figure 7. The as-deposited M1 film showed a more hydrophobic nature in contrast with the CuM1 film. After gas exposure, both surfaces became less hydrophobic, although the contact angle change for the metal-free film was 17° , while for the CuM1 surface was only 3° .

3.2 DFT results

The optimized structures of the M1, CuM1 and gas molecules were used as starting configuration for the gas interaction. The geometric optimizations and gas interaction images obtained

by using DFT calculations are shown in figure 8. In the porphyrin M1 and CuM1 cases, the macrocycle ring exhibited a planar configuration with the radial substituents (phenyl groups) tilted 70° with respect to the average plane of the macrocycles.

The metal-free and copper porphyrin molecules interacting with one NO_2 showed the absorbance of the gas above one of the inner nitrogen groups with a binding energy of $-71.68\ \text{kJ mol}^{-1}$, while in the copper porphyrin case, the gas remained above the central metal atom with a binding energy of $-10.63\ \text{kJ mol}^{-1}$. In both cases, the gas oriented with the nitrogen group towards the porphyrin plane.

The geometric optimization of two metal-free and two copper porphyrin molecules showed that the two metal-free molecules were aligned parallel to each other with a distance of $5.5\ \text{\AA}$, but with a slight offset between them was $2.6\ \text{\AA}$ as seen in figure 8a. In contrast, the copper molecules exhibited a better columnar like alignment. The distance between molecules was $5.0\ \text{\AA}$, while the offset between them was only $0.3\ \text{\AA}$ as shown in figure 8b. As gas molecules were introduced in the simulations between the dimeric systems, the separation between parallel molecules increased regardless of the coordination state of the porphyrin ring. For instance, the

Figure 5. UV-vis spectra of films before and after gas exposure for the (a) metal-free (M1) and (b) copper porphyrin films.

separation between copper molecules reached $5.50 \text{ \AA}$ with NO_2 , while the metal-free system reached $6.02 \text{ \AA}$ after gas insertion. From these results, it is clear that the gas increased the separation between porphyrin planes. In addition, the planarity and the vertical molecular arrangement remain very similar for the metal-free system (figure 8c), while for the copper arrangement (figure 8d), the planarity as well as the columnar alignment were highly disrupted because of the gas molecular interactions with the central metal atom.

On the other hand, preliminary TD-DFT calculations indicated that the UV-vis spectra for the metal-free and copper films showed a small bathochromic shift in the Soret peak after gas interaction in agreement with the experimental results. From our findings, this effect was mostly related to the adsorption of NO_2 groups on the porphyrin ring close to meso-carbon positions, modifying the electronic distribution of the macrocycle ring.

4. Discussion

Some results suggested that porphyrin films exposed to NO_2 can recover over time by exposing the surfaces to elevated temperatures [9] or by flushing and pumping the gas chamber for additional measurements [15]. From our results, not only an irreversible damage of the film surfaces was observed, but

Figure 6. Electrical conductivity of the films during gas exposure at different gas concentrations: (a) metal-free porphyrin (M1) film and (b) copper porphyrin (CuM1) film.

Figure 7. Contact angle of the films before and after gas exposure at 80 ppm: (a) metal-free porphyrin (M1) film and (b) copper porphyrin (CuM1) film.

also different interaction phenomena were identified in terms of the type of central metal atom. For instance, the films with the metal-free centre showed the absorption of gas, while the

Figure 8. DFT configurations for the two-molecular systems with and without NO₂: (a) metal-free porphyrin arrangement, (b) copper porphyrin (CuM1) arrangement, (c) metal-free porphyrin arrangement with NO₂ and (d) copper porphyrin (CuM1) arrangement with NO₂.

copper film showed the degradation of the film at the interface. In both cases, an irreversible damage occurred from the surface downwards.

The morphological results are consistent with the conductivity behaviour. As the gas penetrates inside the metal-free film, the conductivity pathways are truncated because of the presence of pores, which affects the charge mobility and therefore the overall conduction of the film. For the copper system, the gas insertion highly disrupted the molecular packing, which increased the film surface area preventing the gas from being absorbed within the film. Although the roughness values were similar in both cases, the metal-free film showed the largest vertical distance at the value of interface, which probably increase the contact angle.

The UV–vis spectra of the metal-free system showed Soret bathochromic shifts related to the absorption of the gas on the macrocycles, in particular on meso-carbon positions, which modified the electronic distribution of the molecule as a result of the oxidation process. In addition, the reduction of the Soret peak intensity became important, since the gas penetrated through the film oxidizing more molecules as the concentration increased. The absorption of gas within the film was inferred because of the size of the 678 nm peak increased as the gas concentration augmented. In the copper system, the broadening of the Soret peak can be attributed to the overlap of molecules due to molecular misalignment. The position of the Soret peak barely changed since the macrocycle ring remains unaffected. In this case, the main gas-molecular interaction took place between the NO₂ molecule and the central metal atom. On the other hand, the small size of the 686 nm peak for the copper

system can be attributed to the low gas content within the film.

5. Conclusions

In this work, metal-free and copper(II) 5,10,15,20-tetrakis (-4-(methyl 2-phenoxyacetate)) films were employed as NO₂ gas sensors. The UV–vis absorption spectra showed bathochromic shifts due to the porphyrin ring deformation and gas interactions with the macrocycle. From the morphological images, the metal-free porphyrin interface showed the presence of pores, while the copper porphyrin film exhibits surface degradation, showing that the presence of the central metal atom modifies the gas absorption process. Contact angle results showed the reduction of the hydrophobic nature of the films after gas exposure, which can be attributed to changes in the morphology of films in agreement with AFM results. The conductivity response of the films increased as the gas concentration augmented for both cases, although the largest conductive response was for the copper porphyrin system, since it retained most of its bulk integrity after gas exposure. All experimental findings were consistent with DFT and TD-DFT computational results. In addition, it is possible to use porphyrin films as gas sensors, but one must be aware of the degradation of the film after exposure in addition to considering the differences in the gas-film interactions depending on the presence and nature of the central metal atom and peripheral ligands. Finally, evaporated porphyrin films are a better alternative to design chemical sensors to extend the useful life of the device.

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