

Gas effect on the surface photovoltage of porphyrin functionalized ZnO nanorods

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ABSTRACT

Recent studies suggest that the gas sensitivity of porphyrin-functionalized ZnO nanorods can be activated under visible light illumination. Then the use of properly coloured light tuned to the absorbance spectra of individual porphyrins could enable a control of sensors sensitivity. The effect of light on the sensitivity to gases is critically governed by the transport phenomena of electronic charge across the interfaces of organic and inorganic structures. Therefore, accurate measurements of energy levels and contact potential differences in porphyrins functionalized ZnO nanorods are important to interpret the sensing properties of such hybrid materials. For the scope, Kelvin probe measurements of porphyrin-ZnO structures were performed exposing the material in dark and visible light and to organic vapours. Results provide an experimental basis to understand the mutual effects of gas adsorption and illumination to the device conductivity. Copyright © 2012 VBRI press.

Keywords: Organic-inorganic hybrid; ZnO nanorods; microdrop; porphyrins; kelvin probe.

Introduction

The study of the interface properties of organic molecules and inorganic semiconductors is becoming a key topic in materials science mainly because of potential of application like energy conversion [1], optoelectronics [2] and chemical sensing [3]. Properties at the interface are governed by the interaction between the molecular electronic orbitals and the semiconductor energy bands. In the most interesting cases, electrons transfer between the two systems takes place resulting in a distortion of the semiconductor energy bands at the surface. The occurrence of the electron transfer between the molecule and the semiconductor depends on the relative position of the semiconductor Fermi level and the molecular orbitals. However, in order to obtain an effective electronic transfer the organic molecule is requested to be endowed with a proper functional group establishing a chemisorption interaction with the semiconductor surface. Such anchoring functional groups are them of primary importance to determine the overall properties of the organic-inorganic interface [4].

The contact potential difference is a valuable measurable quantity reflecting most of the properties of the interface. The contact potential between the organic

adsorbed layer and the semiconductor can be accessed by Ultraviolet Photomission Spectroscopy (UPS) [5]. This technique was demonstrated to be sufficiently sensitive to allow the relative positioning of the electrons energy levels of porphyrins adsorbed onto a metal surface [6].

When the investigation is oriented to study the consequence of the exposure either to light (case of photodetectors) or to volatile molecules (case of chemical sensors) the interest is focused on the variation of the electronic properties. For these scopes, the complexity of UPS technique can be released in favor of a simpler tool allowing to evaluate the changes in the contact potential. To this regard, Kelvin probe is a tool with an optimal compromise between experimental complexity and information retrieved. The Kelvin probe is a noncontact method to measure the contact potential difference between a probe gold surface and a sample [7, 8]. The technique developed for metal or semiconductors has also been proven useful to study the contact potential difference of organic thin layers over metals or semiconductors [9-11]. Recently we have been interested in studying the sensing properties of the conductivity of ZnO nanorods coated by layers of porphyrins. The cooperation of porphyrins and ZnO nanostructures gives rise to hybrid structures with

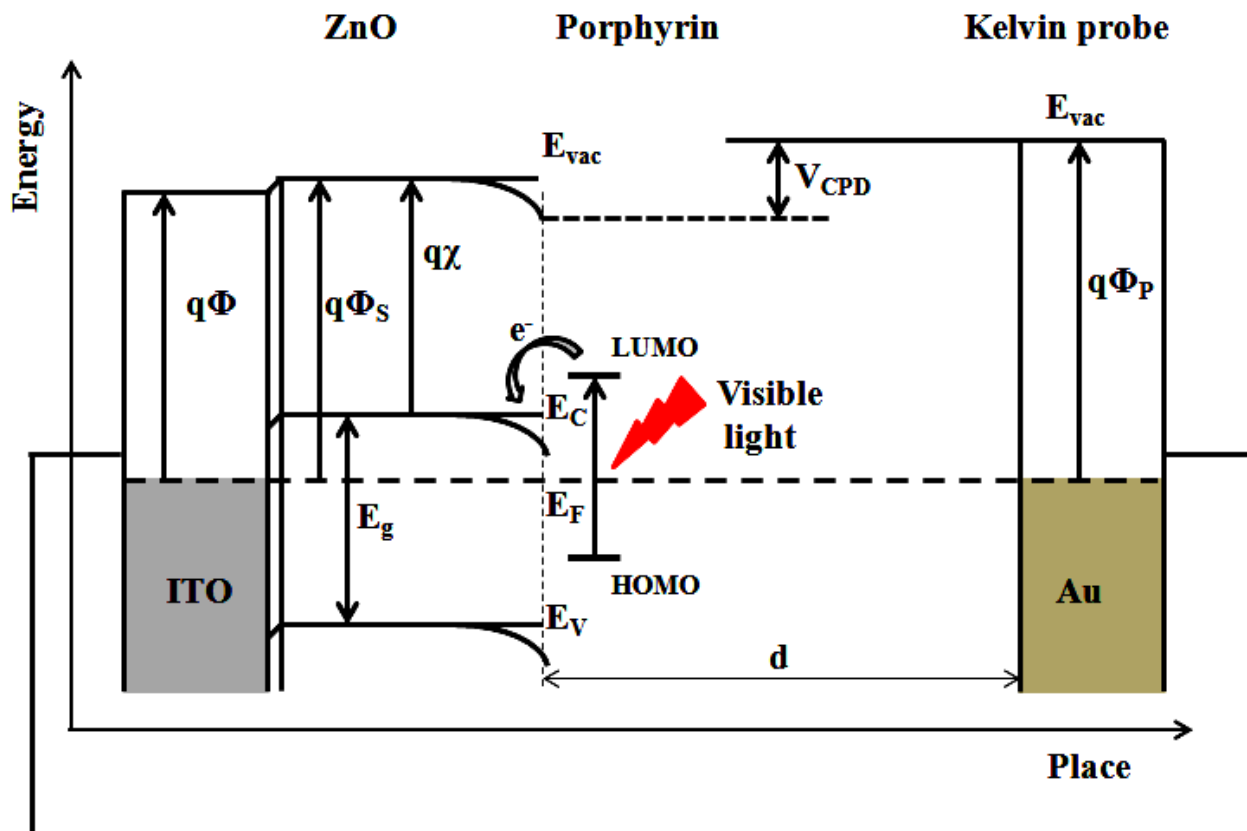


Fig. 1. Energy level scheme and measurement circuit of a Kelvin probe measurement of porphyrin-functionalized ZnO nanorods. The electron transfer pathway in presence of visible light illumination is indicated.

peculiar optical properties, such as enhanced photoconversion [12] and photocatalysis [13].

The application of these properties for chemical sensing has been recently demonstrated in the detection of cysteine in water [14]. We recently observed that the photoconductivity of porphyrins coated nanorods is associated to the photo activation of the sensitivity towards donor species such as amines [15, 16]. The investigation of the surface potential in different light conditions and during the exposure to different volatile compounds is expected to provide information to elucidate the phenomena occurring in the device.

The kelvin probe principle applied to the porphyrin coated ZnO nanorods is shown in **Fig. 1**. ZnO nanorods growth onto a conducting ITO substrate is the tested surface. The Kelvin probe is a conductor probe (a mesh of gold wires in this case) placed at a distance d_0 from the nanorods surface in order to form a capacitor. When sample and probe are electrically contacted by an external connection, the Fermi level equilibrates in the whole system. The equilibrium of Fermi level forces establishes a potential drop between the faces of the capacitor. The potential drop is the contact potential difference and it is equal to the difference of the work functions at the surface of the sample and the probe divided by the electron charge.

In order to get a signal from the biased capacitor, the metal probe oscillates, by means of a piezoelectric actuator.

The distance between the probe and the sample is then modulated according to the following relation-

$$d(t) = d_0 + d_1 \cdot \sin(\omega t) \quad (1)$$

where d_0 is the distance at rest, d_1 is the amplitude of the oscillation and ω is the resonant frequency of the piezoelectric actuator. Due to the time modulated capacitance, and assuming that probe and sample form a plate parallel capacitor the following current flows in the external circuit:

$$i(t) = \frac{dQ}{dt} = \frac{d}{dt} [C(t) \cdot V_{CPD}] = V_{CPD} \cdot \epsilon_0 \cdot A \cdot \frac{d}{dt} \left[\frac{1}{d_0 + d_1 \cdot \sin(\omega t)} \right] \quad (2)$$

where V_{CPD} is the capacitor bias due to the work function difference, ϵ_0 is the air permittivity and A is the area of the probe. This current can be conveniently measured by a number of different electrical setups. Typically the current signal is converted in a voltage signal by a high impedance current to voltage converter, and the current signal is amplified by a lock-in amplifier driven by signal applied to the piezoelectric transducer. By applying an appropriate offset voltage in series to the Kelvin capacitor, the voltage drop over the capacitor can be adjusted to zero, so that the measured current is zero as well. Thus, the offset voltage

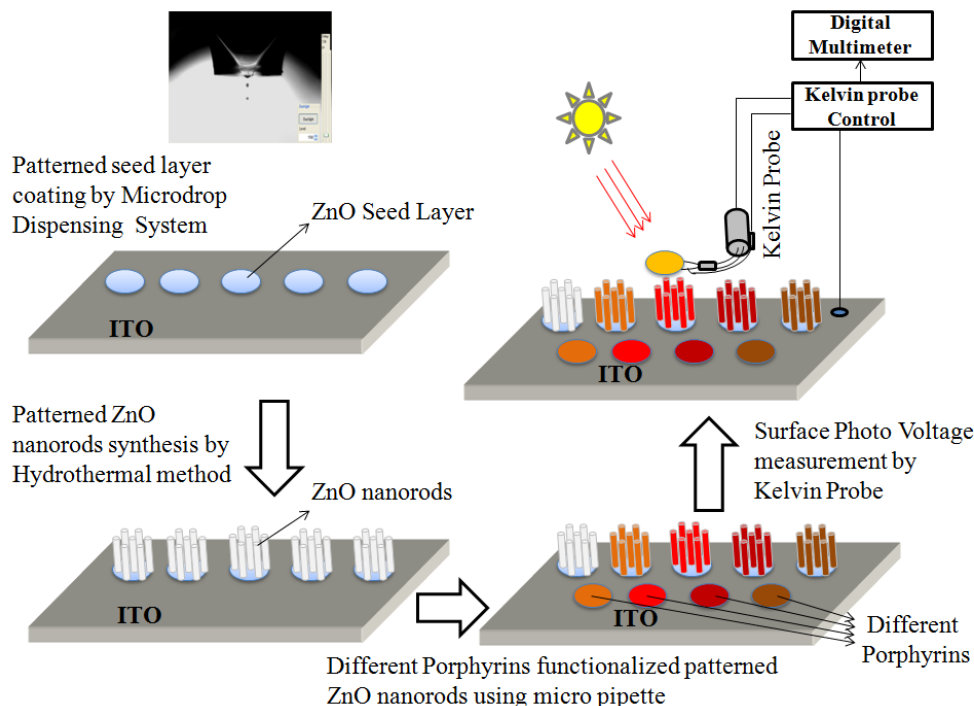


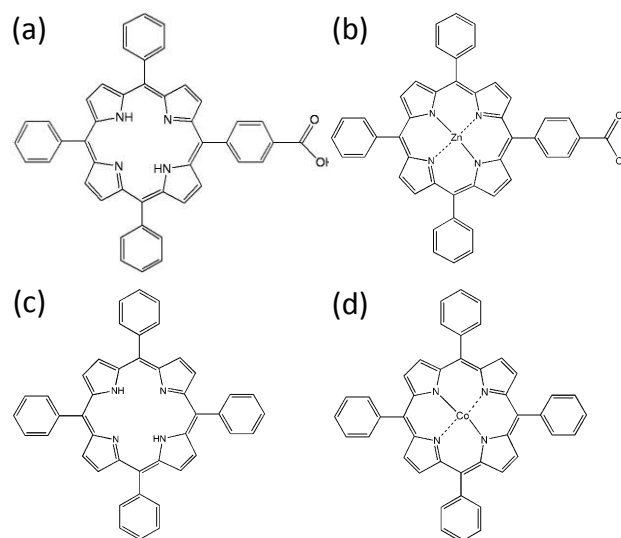
Fig. 2. Pictorial view of the sample fabrication process of patterned and different porphyrin-functionalized ZnO nanorods and typical CPD measurement set-up.

necessary for zero current directly yields the contact potential difference between the sample and the gold probe [17]. In this paper the Kelvin probe is used to study the changes of the surface potential in porphyrins coated ZnO nanorods exposed simultaneous to light and to volatile compounds. Results illustrate the role of the porphyrin functional group allowing for chemisorption of porphyrin onto ZnO surface and the different role played by the nature of the volatile compounds. To understand the transport phenomena of electronic charge across the interfaces of organic and inorganic structure, Density Functional Theory (DFT) modelling of 5-(4'-carboxyphenyl)-10,15,20-triphenylporphyrin (H_2TPPCO_2H) and its complexes with triethylamine and ethanol was performed

Experimental

Contact potential difference has been measured with commercial Kelvin probe equipment provided by Besocke GmbH. It consists in a gold pad of 3mm diameter actuated by a piezoelectric element at a swinging frequency of 180 Hz. The Kelvin probe was mounted on a micrometric screw, allowing a linear scan along the differently colored porphyrins functionalized patterned ZnO nanorods sample. The Kelvin probe is driven by an electronic system allowing for an automatic measurement of the contact potential difference. The output voltage was measured with a multimeter (Hewlett Packard 34401A). Reagents and solvents (Sigma-Aldrich, Fluka and Carlo Erba Reagenti) for synthesis and purification were of synthetic grade and used as received. 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (H_2TPPCO_2H), [(5-(4-carboxyphenyl)-10,15,20-triphenylporphyrinate)]Zinc ($Zn-TPPCO_2H$), 5,10,15,20-tetraphenylporphyrin (H_2TPP) and [5,10,15,20-

tetraphenylporphyrinate]Cobalt (Co-TPP) were prepared as previously reported [18]. Molecular structures are shown in **Scheme 1**. Zinc acetate dehydrate ($Zn(Ac)_2 \cdot 2H_2O$, Sigma-Aldrich, 99%) and hexamethyltetramine (HMTA, Sigma-Aldrich, 99%). Indium tin oxide coated glass was purchased from Sigma Aldrich.



Scheme 1. Molecular structure of (a) H_2TPPCO_2H , (b) $Zn-TPPCO_2H$, (c) H_2TPP and (d) $Co-TPP$.

Fig. 2 shows a pictorial view of the sample fabrication process and the experimental set-up. In order to achieve a homogeneous and controlled layer of ZnO nanorods it is necessary to deposit a uniform seed layer. For the scope, an automatic dispenser (Microdrop GmbH, model MD-K-140)

with 70 μm diameter nozzle was used to deposit ZnO seed layer to fabricate patterned ZnO nanorods array. The relevant parameters during seed layer deposition were substrate and nozzle temperature, dispensing and drying time, drop counts and control impulse of the piezo actuator [19].

The seed layer solution was formed by zinc acetate dehydrate dissolved at the concentration of 0.0275 g in 25 mL ethylene glycol (which have a maximum viscosity of 16.1 mPas at 25°C). Then the solution was utilized as ink without further purification. ITO substrates were cleaned with surfactant, DI water, isopropanol and then with ethanol in ultrasonic bath for 30 minutes at 55°C respectively. An array of seed layer spots was dispensed to demonstrate the patterning growth of ZnO nanorods. The diameter of dispensed droplets on the substrate was about 80 μm (70 μm at the nozzle). In order to match the Kelvin probe size, spots diameter had to be larger than 3 mm; about 30,000 droplets were necessary to cover the requested area. To avoid interferences in Kelvin probe measurement the spacing between two adjacent spots was kept larger than 3 mm. During the seed layer deposition, the substrates were maintained at 90°C to favour the uniformity of seed layer profiles. Finally, the samples were sintered at 400 °C for half hour in order to form a compact ZnO seeds. After seeding processes, the samples were immersed in 25 mM zinc acetate and hexamethylenetetramine solution for 4 hours in order to grow ZnO nanowires by hydrothermal method [20]. During the process the temperature was kept constant at 90 °C. After the completion of the ZnO growth process, the samples were extensively rinsed at least 3 times in DI water. After the synthesis process the sample was characterized by scanning electron microscope (SEM) (Cambridge 360 Microscope (LaB₆), U.K) to ascertain crystallinity and morphology.

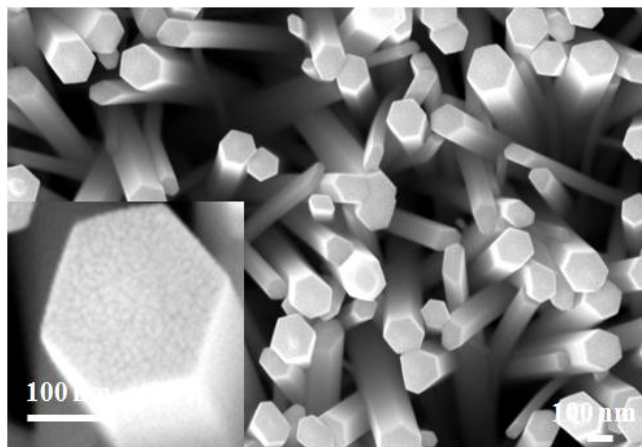


Fig. 3. SEM image of Zn-TPPCO₂H functionalized ZnO nanorods top view.

The synthesized patterned ZnO nanorods on the ITO substrates were functionalized by casting deposition (using micro pipette) of H₂TPPCO₂H, Zn-TPPCO₂H, H₂TPP and Co-TPP dissolved in proper solvents respectively; after drop coating, the nanorods were allowed to dry at room temperature around 1 hour. After coating, the surface of

white ZnO nanorods displayed the proper porphyrin color. **Fig. 3** shows the SEM images of porphyrins functionalized ZnO nanorods. SEM images show a compact coverage of the porphyrins onto the nanorods surfaces. Spectral absorbance of pure and porphyrins functionalized ZnO nanorods were measured with a Varian Cary 500 UV-Vis Spectrophotometer. 1W High Power LED Light Source (ASMT-AW00, Avago technologies) was used throughout the Contact potential difference measurements to illuminate the device.

DFT was calculated with Spartan'10 software (wafefunction inc.) running on iMac (2.93 GHz Intel Core i7) running OSX 10.6. DFT was performed with Lee-Yang-Parr gradient corrected electron correlation function (B3LYP) with the 6-31G* basis [21].

Results and discussion

Patterned ZnO nanorods grew vertically and well aligned on ITO substrate. SEM analysis indicates that ZnO nanorods belong to wurtzite structure and the hexagonal face-cut demonstrates that the material was grown along the c-axis direction (Fig. 3). According to SEM images nanorods diameter was in the range 100-200 nm.

The patterned ZnO nanorods were successively functionalized with layers of H₂TPPCO₂H, Zn-TPPCO₂H, H₂TPP and Co-TPP respectively (**Scheme 1**). The first two porphyrins were functionalized with a carboxylic group in one of the phenyl group in order to improve the anchoring on the ZnO surface. To investigate the role of the anchoring group, two unfunctionalized porphyrins were also used. These molecules are likely to be physisorbed on the ZnO surface. The morphology of porphyrins coated ZnO is observed by SEM image (**Fig. 3**). Porphyrin layers completely coat the ZnO surface both along the walls and the hexagonal face-cuts.

An insight about the interaction between porphyrins and ZnO nanorods can be obtained by the optical absorbance spectra in the visible region. **Fig. 4a** shows the absorption spectra of (1) H₂TPPCO₂H, (2) Zn-TPPCO₂H, (3) H₂TPP, and (4) Co-TPP in solvent phase. The H₂TPPCO₂H and H₂TPP in solvent phase shows the typical dominant Soret band at 418 nm and 419 nm (because both are free-base porphyrins) and the less intense Q-bands between 500 nm and 700 nm. The main difference among these two porphyrins is the anchoring group (-CO₂H). In the case of metalloporphyrins, the Soret band is red-shifted of about 10 nm. For Zn-TPPCO₂H the Soret band peak is at 421 nm, and for Co-TPP the Soret band peak occurs at 431 nm. **Fig. 4b** shows the absorption spectra of (1) pure ZnO nanorods, (2) H₂TPPCO₂H onto ZnO, (3) Zn-TPPCO₂H onto ZnO, (4) H₂TPP onto ZnO and (5) Co-TPP onto ZnO. The UV absorption peak of ZnO has tail in the visible range; otherwise the material is basically transparent. The H₂TPPCO₂H and H₂TPP on ZnO nanorods show the typical dominant Soret band at 435 nm (because both are free-base porphyrins) like solvent phase. But, a significant line broadening and red shift about 16 nm with respect to solvent phase. At the same time, Zn-TPPCO₂H and Co-TPP on ZnO nanorods showed the Soret band at 406 nm and 443

nm respectively. In the case of Zn-TPPCO₂H on ZnO the line broadening and blue shift about 15 nm with respect to solvent phase, for Co-TPP onto ZnO about 12 nm red shifted. These results suggests, there are two different way of porphyrin aggregation on the ZnO nanorods surfaces according to anchoring group and central metal atom. So, the absorption spectra of porphyrins functionalized ZnO is completely due to the presence of the surface porphyrins layer.

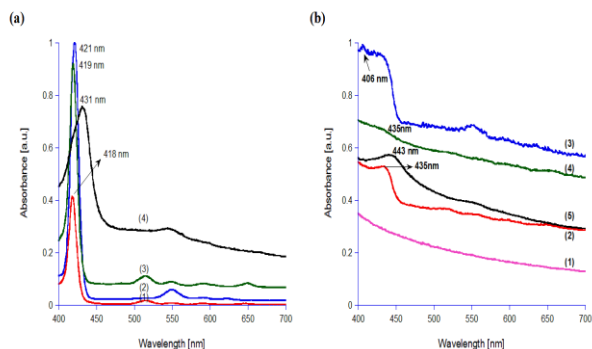


Fig. 4. a) Absorption spectrum of H₂TPPCO₂H, Zn-TPPCO₂H, H₂TPP and Co-TPP in solvent phase. b) Absorption spectrum of Pure ZnO nanorods, H₂TPPCO₂H onto ZnO nanorods, Zn-TPPCO₂H onto ZnO nanorods, H₂TPP onto ZnO nanorods and Co-TPP onto ZnO nanorods.

To put in evidence the properties of the porphyrin-ZnO hybrid, the same porphyrins were also deposited onto the ITO substrate. Typical Kelvin probe measurements are shown in **Fig. 2** with the ITO substrate exposed to ambient air. The CPD signal indicates that the work function is 0.5 eV less than that of the gold vibrating probe. **Fig. 5a** shows the workfunction change of different porphyrins on ITO substrates in dark and light. The absolute value of the work function has been calculated assuming a gold work function of 5.1 eV [22]. According to the results, porphyrins with -CO₂H group shows a dramatic change in work function due to visible light illumination. It reveals the importance of anchoring group to transfer the photoexcited electrons from porphyrins to ZnO.

It is important also to consider the role of the central metal atom of the metalloporphyrin molecule. In case of chemically anchored porphyrins, the work function of Zn-TPPCO₂H is twice the value exhibited by correspondent free base porphyrin: 315 meV for the free base and 646 meV for the porphyrin with the zinc atom. On the other hand, in the case of physisorbed molecules, the addition of the cobalt atom achieves a slight increase of the work function, from 315 meV for the free base to 170 meV for the porphyrin with the cobalt atom.

A full understanding of these results is hindered by the fact that different metals were used. Nonetheless, the addition of the metal atom usually results in a modest increase of the molecular dipole (considering that due to the molecular symmetry the electric dipole of free base porphyrins is small). On the other hand, the large increase of the work function in case of zinc porphyrin can be explained as a consequence of the change of the molecular orbital. The change of orbital energies is well understood considering the different color of the metalloporphyrins, and that an increase of absorbed light results in an increase

of the transferred electrons towards the ZnO. This small change in work function is probably due to slight dipole change in the surface. These results suggest two different photo sensing mechanism among the metal-free and metallo porphyrins. **Fig. 5b** shows the change of the work function of porphyrin-functionalized ZnO nanorods on ITO substrates measured in ambient air, and in presence of vapors of ethanol and triethylamine dissolved in ambient air. In all cases measurements were performed in dark and in light. In ambient air the work function change is quite similar to that observed for the porphyrins on ITO. The effects of the hybrid materials evidently appear exposing the materials to visible light.

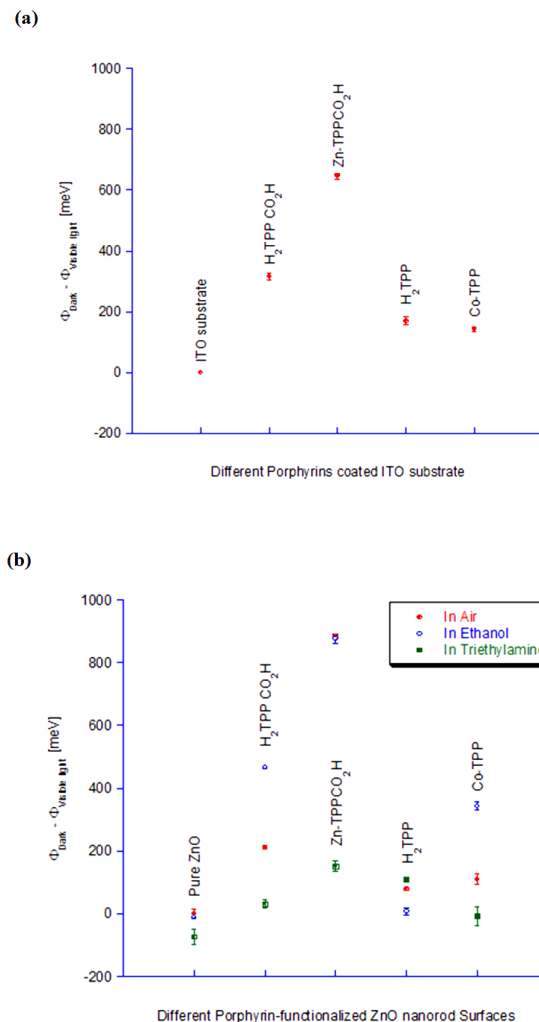


Fig. 5. a) Workfunction change of different porphyrins on ITO substrates using Kelvin probe in dark and visible light. b) The change of workfunction of different porphyrin-functionalized ZnO nanorods on ITO substrates measured in ambient air, and in presence of vapors of ethanol and triethylamine dissolved in ambient air under different light condition.

In this case, the exposure to gas enhances the work function changes of porphyrins functionalized with the carboxylic group. Previous studies shown that the photoconductivity of chemisorbed porphyrins onto ZnO is strongly improved by the exposure to donor compounds, such as amines [16]. The concordance between photoconductivity and Kelvin probe studies demonstrates the effective interaction between porphyrins and ZnO, and

that adsorption phenomena in porphyrins elicit changes of ZnO properties. Noteworthy, Kelvin probe data confirm that chemisorption, prompted by the carboxylic group, is necessary to elicit the charge transfer from porphyrin to ZnO.

On the other hand, the porphyrin behaviour is strongly dependent on the metal atom characterizing the metalloporphyrin complex. However, the phenomena occurring in the porphyrin have a variable influence in the contact potential difference according to the occurrence of electron transfer. For instance the photovoltage in Co-TPP coated ZnO is slightly larger than that occurring in H₂TPP coated ZnO, while the photovoltage of Zn-TPPCO₂H coated ZnO is about four times larger than the photovoltage of H₂TPPCO₂H coated ZnO.

Without the occurrence of electron transfer, both the effects of exposures to light and volatile compounds are confined to the porphyrin layer and affect the Kelvin probe signal only through a change of the surface dipoles layer. Since electric dipoles are vectors, not perfect alignment of porphyrins onto the ZnO surface leads to a small total electric dipole, and then the observed signals are modest. On the other hand, when electron transfer from porphyrin to ZnO is possible, photoexcited electrons and electrons transferred from the donating adsorbed molecules are transferred into the ZnO producing a surface band bending that produces a large contact potential difference.

In order to elucidate this observed hypothesis to volatile organic compounds the structure of H₂TPPCO₂H and its complexes with triethylamine and ethanol were studied with Density Functional Theory (DFT) simulations. DFT models were performed at B3LYP level using the standard all-electron 6-31G* basis for all atoms. Calculus was performed with the Spartan 10 software (from Wavefunction Inc.).

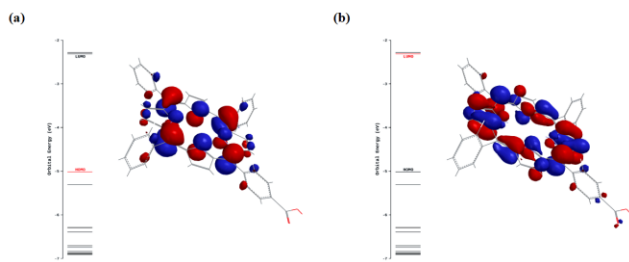


Fig. 6. Density Functional Theory (DFT) modelling of H₂TPPCO₂H: a) Distribution of HOMO level. The calculated energy of the orbital is -5.04 eV. b) Distribution of LUMO level. The energy of the orbital is -2.26 eV.

DFT calculus shows that the the distribution of HOMO level and LUMO level in **Fig. 6a** and **b**. The calculated energy of the orbital of HOMO level is -5.04 eV and LUMO level is -2.26 eV. The shift between HOMO and LUMO is in good agreement with the observed experimental value of 419 nm (**Fig. 4**). The LUMO level is extended to the carboxylic group where the binding with the surface of ZnO nanorods is supposed to take place. Considering that the conduction band of ZnO lies at about -3.7 eV [23] this situation is expected to favour, the injection of photoexcited electrons from H₂TPPCO₂H to ZnO. LUMO level of H₂TPPCO₂H partially covers the carboxyl group anchored on the ZnO nanorods surface which making

possibility to transfer the photoexcited electrons to the ZnO conduction band.

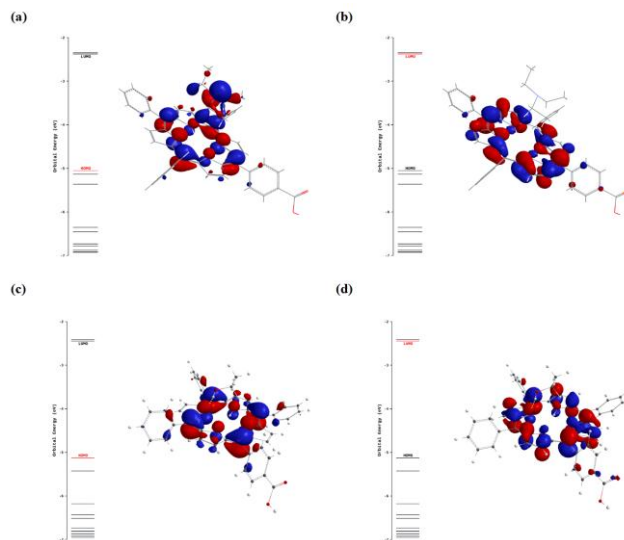


Fig. 7. Density Functional Theory (DFT) modelling of H₂TPPCO₂H with triethylamine and ethanol: a) HOMO distribution in the H₂TPPCO₂H + Triethylamine complex. b) The distribution of the LUMO level of the H₂TPPCO₂H + Triethylamine complex is substantially similar to that of Figure 6b. c) HOMO distribution in the H₂TPPCO₂H + ethanol complex. d) LUMO distribution in the H₂TPPCO₂H + ethanol complex.

Fig. 7a shows the HOMO level distribution in the H₂TPPCO₂H + Triethylamine complex. The level of HOMO is calculated at -5.41eV. The HOMO level covers both the porphyrin aromatic ring and the triethylamine indicating a conjugation of the electron density between triethylamine and porphyrin. **Fig. 7b** shows the distribution of the LUMO level of the H₂TPPCO₂H + Triethylamine complex is substantially similar to that of **Fig. 6b**. In particular the LUMO level is still extended onto the carboxylic group anchoring the porphyrin to the surface of ZnO nanorods. Eventually, electrons shared by porphyrins and triethylamine in the HOMO level are photo-excited in the LUMO level and brought in a region close to the ZnO surface where they can be injected in the ZnO conduction band lying in a favorable energy level.

Triethylamine is a strong electron donor lying almost at the extreme of the Lewis basicity scale [24]. Previous experiments with phthalocyanines, a molecule similar to porphyrins, demonstrated that the resistance change of a layer of metal-free phthalocyanines decreases as a consequence of the exposure to triethylamine vapors. Furthermore, the sensitivity is correlated with the hydrogen bond basicity term [25]. Then it is reasonable to assume that electron transfer may happen also between the systems here investigated and that the triethylamine binds to H₂TPPCO₂H via a hydrogen bond where the triethylamine acts the basic counterpart. However, it is known that Van der Waals interactions are not negligible in triethylamine, then cooperation among different interaction mechanisms can actually takes place.

Fig. 7c shows the HOMO level distribution in the H₂TPPCO₂H + ethanol complex. Ethanol binds to one of the nitrogen of the porphyrin core. In the interaction the ethanol acts as the acid. The HOMO distribution is little

changed with respect to that of Figure 6a and most important it is not extended to the ethanol molecule. This shows that no electron density conjugation takes place between ethanol and porphyrin. The HOMO energy level is -5.12 eV.

Fig. 7d shows the LUMO level distribution in the H_2TPPCO_2H + ethanol complex. The distribution is practically similar to that of **Fig. 7a**. The LUMO energy level is -2.45 eV. In spite of the slight shift the HOMO-LUMO gap remains unaltered with respect to the case of H_2TPPCO_2H and H_2TPPCO_2H + triethylamine. Ethanol is known to be a weak acid and basic compound. Previous observations with porphyrins coated quartz microbalance shown that in free-metal porphyrins the binding of ethanol is favoured with respect to triethylamine [26]. This is due to the direct hydrogen-bond interaction ($OH^+ \cdots N^-$) between the OH group of the alcohol and one of the nitrogen atoms of the porphyrin core.

Conclusion

In this paper we have reported the Kelvin probe characterization of porphyrins coated ZnO nanorods. This couple of materials is usually investigated for their photovoltaic properties but they are also interesting for gas sensing. The combination of sensitivity to light and gases offers the possibility to develop devices with photo-assisted gas sensitivity. For example, the use of different porphyrins with distinct absorbance spectra can enable a selective turning on of the chemical sensitivity. Here we investigated their contact potential differences of porphyrins-functionalized ZnO nanorods under different light condition in ambient air and in atmospheres containing either ethanol or triethylamine vapors. Results indicate that in the case of chemisorbed porphyrins onto ZnO the exposure to light and gas strongly influences the contact potential difference. This result confirms the previously observed relationship between conductivity and exposure to gases and visible light. DFT modelling show that: H_2TPPCO_2H LUMO level distribution is compatible with observed injection of photoexcited electrons into ZnO nanorods. The binding of triethylamine results in a conjugation at the HOMO level of the electron densities of H_2TPPCO_2H and triethylamine, corroborating the observed increase of Photoexcited electrons injected in ZnO nanorods. The binding of ethanol does not result in an electrons density exchange between ethanol and H_2TPPCO_2H , porphyrins coated ZnO should be non-sensitive to ethanol. In both cases, HOMO-LUMO gap remains unaltered. Eventually, Kelvin probe is confirmed as a powerful tool to characterize the sensitivity to light and gases and their combined effects. This tool can be conveniently utilized to optimize the choice of materials to be implemented in devices such as chemical sensors, photo detectors and photo energy converters.

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