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The effect of NO_2 on spectroscopic and structural properties of evaporated ruthenium phthalocyanine dimer

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Abstract

The chemical interaction between NO_2 gas and dimeric ruthenium phthalocyanine $(RuPc)_2$ (Pc = phthalocyanine ligand) films has been investigated by different techniques: UV–Visible spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and Extended X-ray Absorption Fine Structure (EXAFS). The optical spectra in the Q band region (700–500 nm) registered “in situ” enabled to follow the evolution of the process in real time indicating that a two steps reaction, showing two clear isosbestic points, occurs. The first phase was essentially characterised by: (a) the rapid disappearance of the 608 and 420 nm shoulders; (b) the intensity decrease of the main absorption peak and (c) the appearance of a new adsorption band centred around 510 nm. In the second step the remarkable feature is a further lowering of the main peak with the simultaneous decrease of the new 510 nm absorption. These spectral changes suggested that a chemical reaction occurred between NO_2 and ruthenium phthalocyanine with the formation of a radical species due to the macrocycle oxidation. The kinetics indicates that the adsorption of gas by the evaporated $(RuPc)_2$ film is a complex process involving more than one independent mechanism. XPS and EXAFS spectra collected before and after gas exposure showed that the central metals (Ru) were also involved in the oxidation process. The reversibility of the process has been also tested by treating the films at different temperatures, the original optical spectrum being not completely recovered.
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Keywords: Phthalocyanines sensors; Optical spectroscopy; X-ray Photoelectron Spectroscopy (XPS); Extended X-ray Fine Structure (EXAFS)

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1. Introduction

MetalloPhthalocyanines are extensively investigated as weakly semiconducting organic materials for different potential applications [1] due to their unique electrical and optical properties. In particular the study on sensing properties of films is in continuous progress because the absorption and desorption of gases that behave as electron acceptors (NO_2, O_2, halogens) changes the conductivity and the optical properties by making these molecular systems promising for producing cheap and sensitive electronic gas sensors [2]. Many basic aspects need to be considered and examined in order to understand and improve the performance towards NO_2 gas in terms of sensitivity and response time. Much discussion took place in the literature on the role played by the planarity of the molecule in affecting the capability of gas detection. Experimental results showed that planar derivatives, as CuPc or NiPc (Pc = phthalocyanine ligand), are less sensitive than non-planar ones, as PbPc, and that a molecular arrangement parallel to the substrate surface is more effective than other possible orientations [3]. As extension of the work, we investigated, as NO_2 sensors, phthalocyanine compounds containing more than one ring or metal, such as sandwiches and dimers, being their redox properties much different than monomeric species. We first investigated the titanium bisphthalocyaninato $Ti(Pc)_2$ molecule, “a stapled sandwich”, [4,5] and then the dimeric species $(RuPc)_2$, here reported. In a preliminary study [6] we observed that the sensing

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behaviour of $(RuPc)_2$ films towards NO_2 (0–100 ppm) yielded poor results in terms of reversibility, even at very low concentrations. Therefore, we addressed our study to a deep and detailed comprehension of the interaction mechanism between $(RuPc)_2$ film and NO_2 gas, with the aim to establish the role of the two Ru atoms and of the two macrocycle rings, both factors being closely connected to the performance and reversibility of the system. Before the results' discussion, some fundamental structural features of the examined compound should be recalled. The ruthenium phthalocyanine molecule can be isolated only as a dimer, as previously reported [7]. Large Angle X-ray Scattering structural investigation, performed both on bulk and films [8], showed short Ru–Ru bonds (2.40 Å) and a peculiar molecular arrangement consisting in a superimposed organization of the molecular units (6 for the bulk, 11 for the film) along the stacking direction, parallel to the Ru–Ru bonds. This supramolecular aggregation certainly could affect the gas diffusion [9]. Furthermore, it should be taken into account that the interaction with the NO_2 molecule could involve both the macrocycle system and the metals, thus leading even to severe molecular rearrangement. In this perspective we have chosen experimental conditions (NO_2 concentrations and thickness of films) different from those one commonly used for the characterisation of the films as sensors. Structural investigation by Extended X-ray Absorption Fine Structure (EXAFS) technique and surface characterisation by X-ray Photoelectron Spectroscopy (XPS) were performed on samples, both before and after exposure to NO_2 gas. UV–Visible spectra were recorded "in situ" during the gas exposure.

2. Experimental details

Films of $(RuPc)_2$ were prepared by vacuum evaporation, as described elsewhere [8]. The substrates used were chosen in consideration of the planned measurements: optical quartz for UV–Visible spectra and glass for EXAFS and XPS measurements. Thin films of 50–100 nm were generally used (500 nm for EXAFS measurements) and their thickness was monitored by an Edwards FTM5 crystal-balance monitor. Visible spectra were recorded on a Cary 5 spectrophotometer using a quartz cell for gas supplied by HELLMA. The film was deposited on one side of the cell and, after the registration of the first spectrum, a flow of NO_2 (92 ppm NO_2 in dry air as vector gas) of 500 standard cc per minute (sccm) was allowed to pass through. The subsequent spectra were recorded at 2/10 min intervals. After gas exposure, the film was purged by a flow of N_2 for 2 h and the final spectrum was confirmed. In order to check the reversibility of the interaction, the exposed sample was heated, under vacuum, at 130 °C first and then at 200 °C for about 1 h, respectively. Optical and XPS spectra were recorded at each step.

EXAFS spectra were measured at Ruthenium K-edge (22,116 eV) at GILDA Italian CRG beamline of European Synchrotron Radiation Facility in Grenoble (France).The typical ring current was about 125 mA and a flux in the order of 10^9 photons/s was available during measures. EXAFS experiments were performed in the dark at liquid nitrogen temperature by recording the fluorescence signal, collected by a plastic detector capped with 100 μm thick aluminium foil, from the phthalocyanine films. Each spectrum spans for 1000 eV above the edge and the k-spacing was kept constant in order to collect at least 500 data points. To test the reliability of the measures two different batches of the ruthenium phthalocyanine complex were prepared and deposited as film with a 500 nm thickness by sublimation on cold glass substrates. Also the gas exposure (92 ppm NO_2 in dry air as vector gas, 500 sccm for 2 h) was performed twice on different samples to gain a better confidence in the data and more than one data set was collected for each sample. The agreement between independent measures was better than 3% averaged on all the structural information. EXAFS data analysis was performed by the EXCURV92 program [10] that is very suitable when aromatic rings are involved. It is, indeed, possible to describe a ring as a single unit using a limited numbers of parameters to describe the ligand up to roughly 5 Å from the ruthenium centre. The same parameters already used for the analysis of the starting dimer [11] were inserted in the present work to fit the experimental data. The four symmetric rings in the ruthenium plane were described as related by rotation around the C4 axis perpendicular to the ligand plane and the ruthenium-bonded α-nitrogen were at fixed distance from the β-nitrogen and the γ-carbons. When the distance between the central absorbing atom and the first shell ligand was varied, the whole ring, as single highly correlated unit, was shifted accordingly and the correlations inside and in between the ring were calculated in order to maintain the overall structure of the phthalocyanine rings. During the fitting the possible displacement of the phthalocyanine atoms from the ruthenium plane was taken in account. This choice makes possible to limit the numbers of parameters necessary to describe the four phthalocyanine rings.

The surface chemical composition of the samples was investigated by XPS analysis in an ultra high vacuum chamber with a base pressure $P < 10^{-7}$ Pa. XPS measures of $(RuPc)_2$ films were performed on the freshly prepared samples and after exposure to NO_2 gas. Photoemission spectra were collected by a VG ESCALAB MkII spectrometer, equipped with a standard Al K_α excitation source ($h\nu = 1486.6$ eV) and a five-channeltrons detection system. Samples were positioned at the electron take-off angle normal to the surface with respect to the hemispherical analyser, which was set to a constant pass energy ($E_p = 20$ eV). The binding energy (BE) scale was calibrated by measuring C 1s peak (BE = 285.1 eV) from the surface contamination. The accuracy of the measured BE was ±0.1 eV. XPS data were collected and processed by using a VGX900 software. After Shirley background subtraction, a non-linear least-square curve-fitting routine was used for the analysis of XPS spectra, separating elemental species in different oxidation states. Relative concentrations of chemical elements were calculated by a standard quantification routine, including Wagner's energy dependence of attenuation length [12] and a standard set of VG ESCALAB sensitivity factors. As widely accepted [13], the standard error of XPS quantification is lower than ±10%. The experimental error of XPS quantitative analysis of the samples (triplicate measurements) did not exceed ±2%.

3. Results and discussion

3.1. EXAFS analysis

EXAFS analysis was performed by using the same model compounds and parameters of our previous investigation of $(RuPc)_2$ as film [14]. A preliminary study on samples treated with NO_2 yielded not satisfactory fit index (F.I.) parameters as for the untreated films, also taking into account the discrepancy between measured and calculated EXAFS spectra. A first important improvement was achieved when ruthenium contribution at 4.46 Å (Ru–Ru extradimer distance) was omitted from the fit. The first shell bond distances and coordination numbers remained mainly unchanged and the fit index significantly decreased by 20% upon neglecting the contribution of the ruthenium atom belonging to the second dimeric unit, everything else being left as in the previous fitting. These findings led us to perform a deeper analysis on the experimental spectra for films treated with NO_2 gas, because the data quality was as good as for the untreated samples. All the attempts to fit the data were checked with the test for significance of the added shell [15]. The fit index underwent a further improvement when one new contribution was added in first shell at a distance compatible with an axial coordination of the ruthenium metal. The best fit obtained for the film treated with NO_2 (F.I. = 1.37) is reported in Fig. 1 and the corresponding interatomic distances are shown in Table 1. A new contribution is present at a distance of 2.198 Å, that is consistent with a NO_2 molecule axially coordinated to the central metal. EXAFS is unfortunately unable to distinguish the contribution between nitrogen and oxygen, with close atomic mass and spectroscopic behaviour [16], and, therefore, does not allow to establish which is the coordinating atom of the NO_2 molecule. Nevertheless, from these results we can deduce that the columnar arrangement of the dimeric units was destroyed, while the Pc rings appear basically unaffected in distance and geometrical arrangement. In addition the coordination of the NO_2 molecule to a ruthenium atom certainly occurred. The fractional coordination number for both the N and Ru atoms indicates that very likely not all the $(RuPc)_2$ molecules are involved with NO_2 interaction. With this respect it must be noted that: (i) the EXAFS coordination numbers are very highly correlated with the Debye–Waller type factors and the error can be easily larger than 10%, especially for outer shells; (ii) because of the film thickness (500 nm) the gas could have reacted only with a portion of the film deposited on the surface, while EXAFS is sampling a deeper portion.

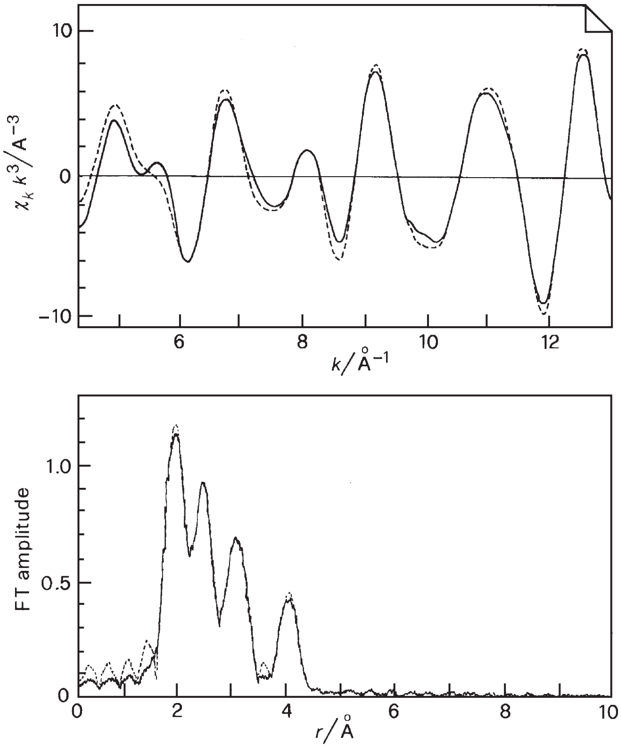

Fig. 1. Experimental (dotted line) and calculated (solid line) $\chi_k k^3$ and below respective Fourier transform for $(RuPc)_2$ film after exposure to NO_2 gas.

Table 1
EXAFS determined interatomic distances (r) in $(RuPc)_2$ film samples after interaction with NO_2 gas

	F.I. = 1.37;R = 18.61		
	n	r (Å)	σ (Å)
Ru–N(A)	4	2.002 ± 0.01	0.055
Ru–Ru(A′)	0.70	2.411 ± 0.01	0.070
Ru–C(A)	4	2.904 ± 0.01	0.118
Ru–C(A)	4	3.020 ± 0.01	0.000
Ru–N(A)	4	3.132 ± 0.01	0.000
Ru–N(A′)	4	3.333 ± 0.01	0.083
Ru–C(A′)	4	4.088 ± 0.01	0.000
Ru–C(A′)	4	4.062 ± 0.01	0.083
Ru–N(NO_2)	1.78	2.198 ± 0.01	0.045

F.I. = fit index; R = residual, ΔE_0 = 15.08 eV; n = coordination number; σ = Debye–Waller type factor; AA′ = Pc ring of the dimeric unit.

3.2. UV–Visible spectra

Fig. 2 shows the complete evolution of the visible spectrum of the $(RuPc)_2$ film during NO_2 exposure (92 ppm, flow = 500 sccm). Two subsequent phases are reported separately and the two isosbestic points appear more evident. The initial spectrum of the evaporated material (Fig. 2b) displays the maximum of Q band at 630 nm with a shoulder at 608 nm and a less evident one at 710 nm, a detailed interpretation of this kind of spectrum can be found in [14]. The final spectrum (Fig. 2c), obtained after about 5 h of gas exposure, can be considered as pointer of the end of the whole reaction between NO_2 gas and the $(RuPc)_2$ film, being the subsequent recordings, in NO_2 flow, perfectly superimposable. The last spectrum, basically characterised by a broader and less intense maximum shifted at 625 nm, a shoulder at 708 nm and a broad absorption centred around 510 nm, was recorded in the same conditions for all the experiments performed, proving the reproducibility of the process. As shown in Fig 2b the most dramatic changes in the spectrum occur during the first step that lasts 90 min. After few minutes of NO_2 gas diffusion, we first observe the disappearance of the shoulders around 608 and 430 nm. Being these small absorptions attributable to the intra-dimers interaction in the solid state [14], the penetration of NO_2 in the core of the stacks

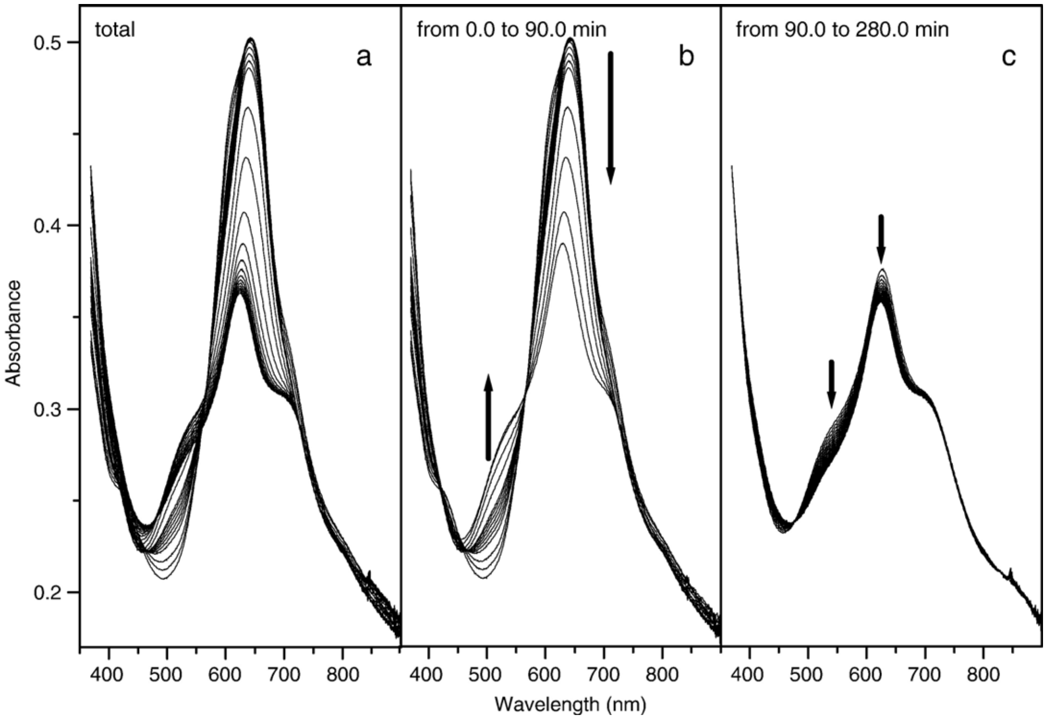

Fig. 2. UV–Visible spectra of the $(RuPc)_2$ film recorded during exposure to NO_2 gas.

brings apart the dimeric units, disarranges the columnar order and gives rise to a more disordered arrangement. This reasonable physical effect is supported by EXAFS data and it would also explain why such absorptions were never recovered by heating the sample (see below).

The other two notable modifications (intensity decrease and shift of the main absorption peak with the corresponding increase of a new peak at 510 nm) are spectral features characteristic of an oxidized form of the phthalocyanine complex, centred on the macrocycle. As already reported [17,18], the appearance of a band around 520 nm and a noticeable decrease of the intensity of the Q band (without shifting) is due to macrocycle restricted oxidation, not involving the metal, in which case shifting of the maximum is expected. The interaction of an acceptor gas as NO_2 with phthalocyanine systems is the topic of the specific literature of chemical sensors, but it is worth to mention that understanding the nature of the bond occurring at the metal and at the macrocycle is not a trivial task and needs a deeper insight. Battisti and Aroca [19] reported spectroscopic results for Langmuir–Blodgett films of $Yb(Pc)_2$ exposed to NO_2. They interpreted the lowering and shifting of the Q band towards lower energy and the presence of the absorption around 500 nm in terms of charge transfer interaction with enough loss of electronic charge in the macrocycle to cause the appearance of a second maximum in the Q band spectral region. A clear lowering of the main adsorption band was also observed for the $Gd(Pc)_2$ sandwich type complex when exposed to chlorine gas and the formation of an oxidized species $[Gd(Pc)_2]^+$ was suggested by the authors also in this case [20]. Our spectroscopic results referred to the first step are in agreement with the expected behaviour for an oxidation process and lead us to state that the NO_2 molecules, permeating through the film, give rise to a radical species also for the dimeric molecule examined. In addition, as firstly anticipated by the EXAFS results and also discussed in the following XPS section, the Ru metal is simultaneously involved in the process through bonding NO_2 molecule. The second step of the process, that takes a longer time of gas exposure up to 280 min, shows a slow backwards of the new 510 nm band that can be explained in terms of depleting of radical population due to the coupling arising from the extensive oxidizing condition. This phenomenon can be compared to the drop of conductivity displayed by bis-phthalocyanine exposed to high concentration of NO_2 and explained by the decrease of mobility of p-type carriers due to their large number [21].

In order to allow the desorption of gas from the lattice, the film was treated at 200 °C under vacuum. The original spectrum and that recorded after the thermal treatment are reported in Fig. 3. The shoulders at 430 and 608 nm are no more recovered, as expected for structural modifications induced in the lattice, and the absorbance at 510 nm is no longer present as evidence of the disappearing of oxidized species.

3.3. XPS analysis

The surface chemical composition of the $(RuPc)_2$ film was determined by XPS, both before and after the interaction with NO_2 gas. The binding energies (BE) of the main XPS peaks and the relative chemical composition of the samples (at.%) are reported in Table 2. In order to discriminate between ruthenium species in different chemical environment, XPS spectra in the (Ru 3d+C 1s) region: 278–292 eV were analysed by a curve-fitting procedure and representative results are shown in Fig. 4. Ruthenium double-splitted components (Ru_1 and Ru_2) are

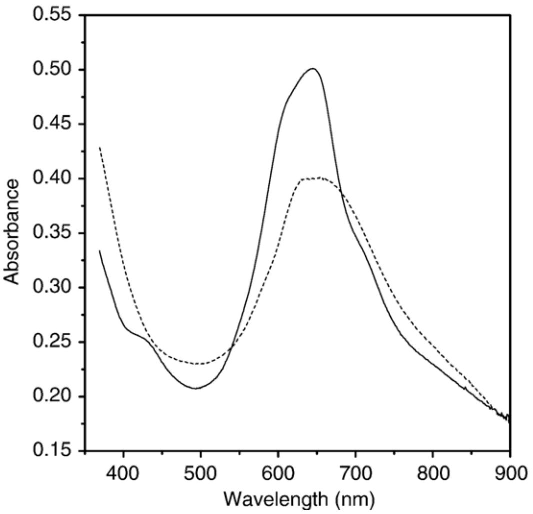

Fig. 3. UV–Visible spectra of the $(RuPc)_2$ film before exposure to NO_2 gas (solid line) and after the thermal treatment of the film exposed for 280 min to NO_2 gas (dotted line).

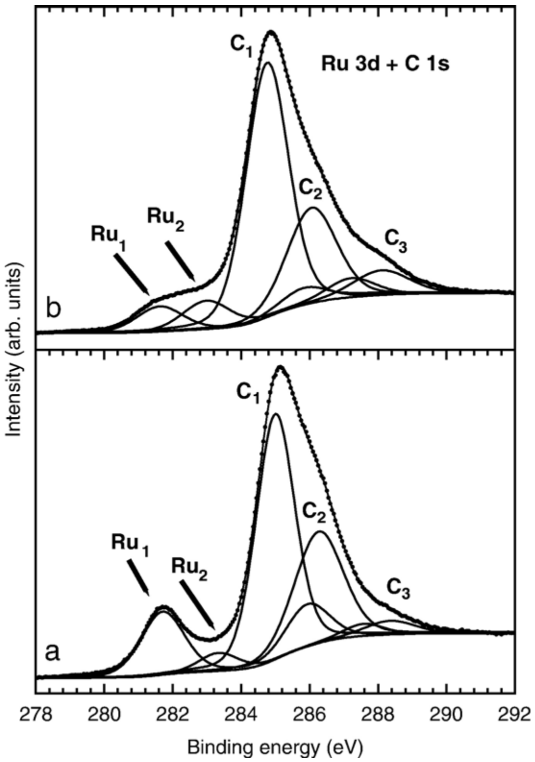

Fig. 4. Curve-fitting of XPS spectra of the $(RuPc)_2$ film before (a) and after exposure to NO_2 gas (b) in the (Ru 3d+C 1s) region. The scattered points refer to the raw data, while the solid line to the fitting results. Ruthenium double-splitted components are marked as Ru_1, Ru_2 and C 1s components are indicated as C_1, C_2, C_3.

plotted as solid lines and C 1s components (C_1, C_2, C_3) are plotted as dotted curves. The Ru 3d spectrum of the freshly prepared $(RuPc)_2$ film (Fig. 4a) is dominated by a major Ru $3d_{5/2}$ component at BE = 281.7 eV (Ru_1 peak), attributable to Ru(II) in the $[RuN_4]$ chromophore group of $(RuPc)_2$ [22,23]. A second Ru $3d_{5/2}$ component located at BE = 283.1 eV (Ru_2 peak) can be assigned to ruthenium species with higher charge density, i.e. in oxidation state higher than (IV) [22,23]. This is not surprising, since a small fraction of Ru oxidized species are very commonly encountered on the surface of ruthenium compounds. A small amount of oxygen was found on the freshly prepared $(RuPc)_2$ film prior to NO_2 exposure, as shown in Table 2, most likely gained during deposition and/or transfer to the XPS spectrometer. The C 1s spectrum can be deconvoluted by the curve fitting procedure into three components: C_1 peak at BE = 285.1 eV, which can be assigned to aromatic species (C atoms in the phenyl rings); C_2 peak at BE = 286.3 eV attributed to pyrrole C atoms and C_3 peak located at BE = 288.5 eV, which can be assigned to shakeup excitation of the C_2 component. XPS spectra recorded after exposure to NO_2 gas show the same Ru $3d_{5/2}$ components as in the $(RuPc)_2$ film but in a different relative ratio. The intensity of the Ru $3d_{5/2}$ spectral feature located at higher binding energy (Ru_2 peak) increases as a function of the exposure to the gas, as shown in Fig. 4b. The oxidative effect of the NO_2 molecule towards Ru atoms can explain the assignment of the Ru $3d_{5/2}$ component at BE = 283.1 eV to Ru oxidized species. The same results in a reference sample of $(RuPc)_2$ powder after NO_2 gas treatment (not shown) unequivocally supports this attribution. A detailed XPS investigation of the absorption of increasing amounts of NO_2 and the gas desorption from the $(RuPc)_2$ film upon thermal treatment are out of the scope of this paper and will be published in a forthcoming paper, but some of the most important results can be anticipated here. XPS spectra were recorded from the $(RuPc)_2$ film: (i) as freshly deposited (step 1); (ii) after exposure to 92 ppm NO_2 in dry air for 1 h (step 2); (iii) after a further exposure to the gas for 1 h (step 3); (iv) after heating the exposed film at 150 °C for 1 h under vacuum (step 4) and (v) after a further thermal treatment at 200 °C for 1 h under vacuum (step 5). The relative distribution of surface ruthenium species as a function of increasing exposure to NO_2 gas (steps 1–3) and subsequent desorption (steps 4–5) is reported in Table 2, as derived from the curve-fitting of the Ru $3d_{5/2}$ photoelectron peak. The ratio between the two Ru components (Ru_2/Ru_1) increases from the initial value of ~0.3 up to 1.0 during the progressive adsorption of NO_2 gas, the latter pointing at a 50% fraction of Ru species completely oxidized on the film surface.

Table 2

Binding energies (BE) of the main XPS peaks and relative chemical composition of the samples (at.%)

Sample BE (eV)	C 1s 285.1	N 1s 399.4	O 1s 533.0	Ru $3d_{5/2}$ 281.7	Ru_2/Ru_1
$(RuPc)_2$ film	78.0	16.3	1.9	3.8	0.27
NO_2 adsorption (step 2)	77.4	14.7	4.4	3.5	0.56
NO_2 adsorption (step 3)	76.6	15.0	6.0	2.4	1.05
NO_2 desorption (step 4)	77.9	11.1	8.4	2.6	0.65
NO_2 desorption (step 5)	75.7	10.5	11.4	2.4	0.76

The relative surface composition of ruthenium species, as derived from the curve-fitting of the Ru $3d_{5/2}$ photoelectron peak, is reported as (Ru_2/Ru_1) ratio.

The value of this ratio progressively decreases as a function of NO_2 gas desorption upon thermal treatment down to ~0.7. It is worth noticing that the (Ru_2/Ru_1) ratio does not recover the initial distribution of ruthenium species in the freshly prepared $(RuPc)_2$ film. This finding suggests that the oxidation of Ru atoms by NO_2 is not a reversible reaction, since a considerable fraction of surface oxidized ruthenium species are left even upon removal of the gas by heating the sample at 200 °C. In order to verify these conclusions, also the more reliable curve-fitting of the Ru $3p_{3/2}$ photoelectron peak was performed, since the Ru $3d_{3/2}$ peak overlaps with the C 1s peak and the (Ru 3d+C 1s) region is particularly crowded. Also in this case a Ru component attributed to the higher oxidation states of Ru, such as Ru (VI) in RuO_3, was found upon NO_2 adsorption and the same surface distribution of ruthenium species as a function of the adsorption/desorption of the gas was determined.

The interaction of NO_2 with the $(RuPc)_2$ film induces modifications also in the N 1s photoelectron signal. In the freshly prepared $(RuPc)_2$ film the N 1s spectrum consists of a major component located at BE = 399.4 eV, as expected for the eight nitrogen atoms in a metal-coordinated phthalocyanine macrocycle [22,24]. A second small component at BE = 400.8 eV accounts for a N–C shake-up transition [24,25]. The N 1s spectrum of the $(RuPc)_2$ film after exposure to NO_2 shows the appearance of a new peak located at BE = 406.4 eV that can be related to the presence of $RuNO_2$ species [22,26]. A minor component at BE = 403.5 eV can be attributed to shake-up satellites ($\pi-\pi^*$) from entrapped NO_x [27]. The intensity of the peak assigned to the new $RuNO_2$ bond increases as a function of the exposure to the gas, thus confirming that NO_2 reacts with the central metal producing ruthenium species at oxidation state higher than (IV).

3.4. Conclusions

The interaction of $(RuPc)_2$ film with NO_2 gas was experimentally evidenced by different spectroscopic studies. The results here shown, together with a very recent gas diffusion study [9], allow us to draw the general observation that we are in presence of a cooperative oxidation process in which both the metal and the macrocycles are interested. We believe that NO_2 gas axially coordinating the ruthenium gives rise to an irreversible change that strongly modifies the chemical nature of the system towards a dimer–monomer transformation. The macrocycle radical, formed by a charge-transfer reaction, appears instead the only species sensitive to the gas presence. In conclusion, the gas–film interaction induces a severe molecular rearrangement, being the initial columnar packing surely destroyed. X-ray structural investigations are in progress in order to get information on the new molecular order and to identify whether oxygen or nitrogen of NO_2 is the coordinating atom to the central ruthenium.

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