Polymer distributed Bragg reflectors for label-free vapor sensing

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**POLYMER DISTRIBUTED BRAGG REFLECTORS
FOR LABEL-FREE VAPOR SENSING**

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2016

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FOR LABEL-FREE VAPOR SENSING**

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A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
Doctor of Philosophy

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Statement of Originality

I hereby certify that the work embodied in this Thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

3rd August 2016
Date

Paola Lova

Abstract

The lack of sensors for extensive, continuous low-cost detection of vapor pollutants is a serious concern for health and safety. Thanks to their low cost and easily interpretable signal transduction, colorimetric sensors, such as polymer distributed Bragg reflectors (DBRs) could achieve this task, but are typically affected by low vapor permeability and lack selectivity without chemical labelling. This thesis demonstrates all-polymer Bragg multilayers for label-free and selective detection of organic volatile compounds achieved employing highly permeable nanocomposites and amorphous poly(p-phenylene oxide) (PPO).

The nanocomposite structures alternate cellulose acetate layers to highly permeable films polystyrene matrices loaded with ZnO nanoparticles. These sensors were fabricated starting from a colloidal solution of nanoparticles fabricated via solvothermal route and modified to increase the affinity with the polystyrene matrix. The inorganic load allows increasing the polystyrene permeability by a factor 3.5 and the DBR sensitivity down to concentration of toluene vapors below 1 ppm. The nanocomposite sensors are able to disentangle among vapors with fairly dissimilar molecular structure, but cannot distinguish between similar molecules such as benzene and toluene.

To selectively detect these vapors, poly (p-phenilenoxide) was implemented as active sensing medium in the DBR sensors. The system exploits the ability of amorphous PPO to uptake large amount of guest molecules and to form co-crystalline phases with distinct optical properties. PPO thin films and DBRs with good optical quality containing both the crystalline and the amorphous phase were demonstrated. The amorphous material is used for the fabrication of DBR sensors showing fast response to toluene vapor. Studies on the selectivity of the system demonstrate its ability to distinguish among vapors of benzene, toluene, *o*-dichlorobenzene and carbon tetrachloride. Infrared spectroscopy investigations prove that the vapor exposure induces the formation of different crystalline

phases within the PPO films, thus allowing the label-free selectivity of the DBR sensor.

These results promise to simplify the detection of volatile organic compound vapors that now requires collection of large amount of air and laboratory analyses. The possibility to evaluate the optical response of the DBR sensors even via the naked eye is promising for the development of lab-on-a-chip devices which can be used by the end users, allowing the extensive and constant monitoring of air quality in environments affected by volatile organic compound pollution.

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Abbreviations

ATR	Attenuated total reflection
BEN	Benzene
CA	Cellulose acetate
CCD	Charge coupled device
CTC	Carbon tetrachloride
DBR	Distributed Bragg reflector
DCB	Ortho dichlorobenzene
DMOS	Methoxy (dimethyl)octadecylsilane
FT-IR	Fourier transform infrared spectroscopy
k	Extinction coefficient
Mw	Molecular weight
n	Refractive index
N	Number of periods
NP	Nanoparticle
PE	Permeability
PhC	Photonic crystal
PM-IRRAS	Polarization modulation-infrared reflection-adsorption spectroscopy
ppb	Parts per billion
ppm	Parts per million
PPO	Poly(p-phenylene oxide)
PS	Polystyrene
R	Reflectance
rpm	Rounds per minute
rps	Rounds per second
SEM	Scanning electron microscopy

T	Transmittance
TE	Transverse electric
TM	Transverse magnetic
TOL	Toluene
VOC	Volatile organic compound
XRD	X-ray diffraction

Chapter 1

Introduction

Volatile organic compounds are increasingly polluting the atmosphere endangering the environment and the human health. Due to their toxicity and the large number of potential sources, extensive monitoring of air quality in working and habitative environments is necessary to preserve people health. This Chapter analyzes these aspects focusing on the figures of merit and requirements for vapor sensors. This analysis allows to define the objectives of this project, which aims to develop new sensors for extensive detection of volatile organic compounds vapors.

Low fabrication costs, ease of manufacturing and of integration in lab-on-a-chip devices make polymer distributed Bragg reflectors interesting for this purpose. When polymers are used as building blocks, strong spectral responses and ease of fabrication promise new generation colorimetric lab-on-a-chip sensors, that can be used without instrumentation. On the other hand, these structures are usually not selective and sensitive to vapor analytes. The last Paragraph of this Chapter describes the approaches used to overcome these limitations and the main outcomes of this Thesis project.

1.1. Motivation

The continuous production and consumption of goods is increasingly releasing harmful chemicals into atmosphere, water sources, and soil. Among these pollutants, volatile organic compounds (VOC) pose serious environmental harm and concern to the human body. The term VOC includes all the organic species with boiling point ranging from 0 °C to ~400 °C. They are further classified into three sub-categories: very volatile (VVOC with $T_{eb} < 50-100^{\circ}\text{C}$), volatile (VOC with $50-100^{\circ}\text{C} < T_{eb} < 240-280^{\circ}\text{C}$) and semi-volatile (SVOC with $240-250^{\circ}\text{C} < T_{eb} < 380-400^{\circ}\text{C}$). Table 1.1 provides a classification of common compounds based on their effect on human body. The list shows that commonly used solvents such as acetone can cause neurological damages, and that tetrachloroethylene, frequently used for dry cleaning, is a suspected carcinogenic agent.^{1, 2}

Table 1.1: List of common VOC based on their effect on human body.

<i>Effects</i>	<i>Compounds</i>
<i>Toxic to organ systems¹</i> (reparatory, cardiovascular, gastrointestinal, reproductive, liver, kidney and skin.)	<i>Toluene, xylenes, chlorobenzene, dichlorobenzenes, styrene, carbon disulfide, acrolein, chloroform, bromoform, 2-butanone, 1,3-butadiene, tetrachloroethane, dichloroethene, chloroethane, dichloropropenes, bromomethan, hydrazines.</i>
<i>Mutagen and developmental¹</i>	<i>Xylenes, n-hexane, ethylene glycol, vinyl chloride, acrylonitrile, acrylamide, ethylbenzene, chloroform, chloroethane, dichlorobenzenes, phalates, ethylene oxide.</i>
<i>Neurological¹</i>	<i>Fuels and mineral oils, toluene, acetone, n-hexane, benzene, xylenes, acrylonitrile, pyridine, trichloroethane, carbon tetrachloride, chloroform, 1,3-butadiene, ethylbenzene, mercaptanes, naphtalenes.</i>
<i>Potential carcinogen²</i>	<i>Polycyclic aromatic hydrocarbons, acrylonitrile, acrylamide, nitrobenzene, styrene, hydrazines, naphtalenes, halogenated hydrocarbons (e. g. chloroform, carbon tetrachloride, dichlorobenzenes, trichloroethylene, hexachloroethane polyhalogenated biphenyles)</i>
<i>Carcinogen²</i>	<i>Benzene, formaldehyde, vinyl chloride, ethylene oxide, benzidine, 1,3-butadiene, bis(chloromethyl) ether.</i>

Indoor VOC pollution causes sick building syndrome³ leading to eye and respiratory irritation, headaches, loss of coordination and nausea.⁴ On the long-term, the exposure can damage liver, kidneys and the central nervous system. VOC poisoning is also linked to the development of cancer.⁵ Moreover, VOC pollution contributes to the formation of tropospheric ozone by reaction with oxygen sources such as nitrogen oxides and carbon monoxide.⁶ Tropospheric ozone is a greenhouse gas contributing to global warming⁷ and a powerful oxidizing agent that causes respiratory illness;⁸ it can also react with other chemical compounds to form new toxic pollutants.⁹

VOC are released by many industrial processes such as oil refinery, power plants, and chemical manufactures, and in urban areas by automotive vehicles, painting works, dry cleaning, refrigerators, wood burning and photocopy machines.^{3, 4, 10}

The high level of toxicity and the wide spreading of these compounds make their identification and extensive monitoring in habitative and working environments critical to preserve people's health and to identify proper treatments in case of poisoning. For this reason, detection methods for extensive VOC monitoring must fulfill four main requirements:

- **Simple measurements and ease of signal transduction**

Detectors for extensive monitoring of VOC pollution should allow un-trained operators to evaluate the air quality in working and habitative environments. Consequently, the detectors must provide easily interpretable data, and allow simple measurement procedures, which does not imply complicated sampling methods and laboratory analyses.

- **Simple fabrication**

VOC can be released in vehicles, household, offices and in many manufacturing plants and working environments. To prevent poisonings, extensive monitoring of all the areas subjected to possible leakages is necessary. Therefore, simple, fast and low cost fabrication methods are required to allow such a large number of devices to be employed.

- **Sensitivity and low detection limit**

While simple fabrication and measurements are always advantageous, other figures of merit may vary depending on the leaking sources. In industrial plants, such as oil refinery and paint manufacturing, VOC sensors require to detect very small concentrations. Indeed, pollutants such as benzene and formaldehyde can lead to carcinogenic effects even in concentration lower than 1 ppm.⁵

- **Selectivity**

In urban and rural environments, the large amount of activities that may release VOC make the identification of pollutants of primary importance to evaluate the risks and the proper treatment in case of poisoning.

As explained in Chapter 2, both established technologies and new concept sensing devices hardly fulfill all these requirements simultaneously. Established qualitative technologies require complicated sampling and laboratory analyses. Conversely, systems for quantitative detection are highly user friendly, but does not allow to discriminate among pollutants. Colorimetric sensors based on the interaction between the analytes and chemical labels do not require instrumentation,¹¹⁻¹³ but the need for chemical targeting increases complexity of data interpretation and do not allow determination of concentration levels. The possibility to achieve selective responses to analytes based on an intrinsic response of the active material could be a paradigm changer, leading to the development of label-free colorimetric technologies for safety devices.

1.2. Objectives and Scope

The scope of this project is to develop sensors for VOC monitoring capable to overcome the limitations of standard technologies and satisfy the requirements described above. This project has four main objectives:

- i. Develop low-cost sensing platforms via easy and fast fabrication.
- ii. Achieve sensitivity to different VOC pollutants.
- iii. Achieve selectivity among pollutants.
- iv. Define a simple transduction system.

Low fabrication costs, ease of manufacturing and of integration in lab-on-a-chip devices make polymer and mesoporous inorganic distributed Bragg reflectors (DBRs)¹⁴ interesting sensing platforms. As discussed in the next Chapter, while inorganic mesoporous vapor sensors have been extensively reported in literature,¹⁵⁻²⁴ they suffer from long fabrication procedures.²⁵ and possess small optical response to the analytes, which often requires complicated data analyses. Contrarily, polymer DBRs are characterized by strong spectral responses and simple fabrication processes such as spin-coating deposition and co-extrusion.²⁶⁻³¹ On the other hand, the low permeability of amorphous polymers hinders their sensitivity to vapors,³² while selectivity has never been reported. The next Paragraph describes the working principle of DBR sensors, the motivation leading us to focus on polymer DBRs, and the approaches used to enhance their sensitivity and achieve label-free selectivity.

1.3. Dissertation

DBRs consist of a lattice of media with different refractive index stacked periodically in one dimension.¹⁴ Reflection and refraction at every interface between these media are responsible for the DBR photonic band structure, which provides a typical optical response. DBRs sensing relies on the modification of such optical response generated by the variation of the lattice effective refractive index and/or periodicity. This variation can be induced by the intercalation of an analyte within the photonic structure. To understand this concepts, it is necessary to explain the phenomena that origin the photonic band-structure and their properties.

1.3.1. The Origin of the Stop-Band

The photonic band structure of a DBR arises from the interaction between the dielectric lattice and electromagnetic waves. This interaction generates forbidden frequencies, where photons cannot propagate within the dielectric lattice, and are diffracted backwards. These ranges of forbidden frequencies are called stop-bands, and are detectable in the DBR spectrum as maxima in reflectance. The stop-band can be described considering the reflection and refraction occurring at every interface for a plane wave propagating across the structure. For sake of simplicity, the normal incidence propagation will be first discussed considering a DBR made by media with refractive index n_1 and n_2 , where $n_1 < n_2$ (Figure 1.1). Our goal is to describe the conditions that generates a maximum of reflectance, which correspond to the stop-band, and consists in the constructive interference between the reflected beams (1_r and 2_r).

Figure 1.1: Scheme of the reflection at normal incidence for a DBR.

There is constructive interference when the beams 1_r and 2_r are in-phase, which means that the difference between their optical path equals their phase displacement. We define the wave-vector for the two media, k_1 and k_2 as

$$k_1 = \frac{n_1 \omega}{c} \quad (1.1)$$

$$k_2 = \frac{n_2 \omega}{c} \quad (1.2)$$

where $\omega = 2\pi\nu$, c is the speed of light in the vacuum and ν is the frequency of the wave. The phase displacements induced by the reflection at the interfaces is given by the optical paths within the media³³

$$\Delta\phi_1 = 2k_1 d_1 + \pi \quad (1.3)$$

$$\Delta\phi_2 = 2k_2 d_2 + 2k_1 d_1. \quad (1.4)$$

Then, the total phase displacement between 1_r and 2_r can be defined as

$$\Delta\phi = \Delta\phi_2 - \Delta\phi_1 = 2k_2 d_2 - \pi. \quad (1.5)$$

The two beams are in-phase when $\Delta\phi$ equals an inter number of wavelength (m)

$$\Delta\phi = 2\pi m. \quad (1.6)$$

Combining equation 1.5 and 1.6, it is possible to define the condition of constructive interference

$$\Delta\phi = \Delta\phi_2 - \Delta\phi_1 = 2k_2 d_2 = (2m + 1)\pi. \quad (1.7)$$

The maximum reflection is obtained for $m = 0$, then

$$2k_2d_2 = \pi. \quad (1.8)$$

Being $\lambda = 2\pi c/\omega$, it is then possible to describe the condition of maximum reflectance for the beam 2

$$d_2 = \frac{\lambda_2}{4n_2}, \quad (1.9)$$

and applying the same elaboration to the beam 1:

$$d_1 = \frac{\lambda_1}{4n_1}, \quad (1.10)$$

where λ_1 and λ_2 are the wavelength generating constructive interference in the medium 1 and 2. This equation indicates that the reflection is maximum when the $\lambda/4$ condition is applied. This take place when the thickness of every layer offers an optical path equals to $\lambda/4$ of the wavelength propagating in the media. In the case of maximum interference, this correspond the photonic stop-band wavelength:

$$n_1d_1 = n_2d_2 = \frac{\pi c}{2\omega} = \frac{\lambda_0}{4}. \quad (1.11)$$

Considering one single DBR period with thickness $D=d_1+d_2$, one can observe that the constructive interference also takes place when the sum of the optical path within the two media equals $\lambda/2$

$$n_1 d_1 + n_2 d_2 = 2 \frac{\lambda_0}{4} = \frac{\lambda_0}{2}, \quad (1.12)$$

which, for a DBR placed in air, assumes the form of

$$D = \frac{\lambda_0}{2n_{eff}} \quad (1.13)$$

where λ_0 is the wavelength of maximum reflection and n_{eff} is the effective refractive index, defined by the effective medium theory³⁴

$$n_{eff}^2 = n_1^2 \left(\frac{d_1}{d_1 + d_2} \right) + n_2^2 \left(\frac{d_2}{d_1 + d_2} \right). \quad (1.14)$$

In the latter case, the reflectance intensity will be lower than in the ideal $\lambda/4$ condition due to a disruptive contribute introduced by the reflection at the odd interfaces.

1.3.2. The Bragg-Snell's Law

The Bragg-Snell 's law is a simple equation that describes the spectral position of the stop-band. It will be widely used to describe the behaviors of DBR subjected to external stimuli. It is then dutiful to explain its derivation.

We consider the diffraction process in a crystalline structure made by equidistant parallel planes, like the one reported in Figure 1.2.

Figure 1.2: Diffraction in a crystalline semiconductor.

In this structure, diffraction peaks are generated in condition of constructive interference, that is when the difference between the optical path $(AO' + A'O') = 2D\cos\theta$ is a multiple of the radiation wavelength, as described by the Bragg's law:

$$m\lambda = 2D\cos\theta \quad (1.15)$$

The law is satisfied when D is of the order of magnitude of the Bohr radius and $\lambda \approx D$. In a photonic crystal, being D comparable with the wavelength of visible light, one needs to consider the refraction occurring at every interface, as described by the Snell's law

$$n_1 \sin \theta_1 = n_2 \sin \theta_2. \quad (1.16)$$

This phenomenon is illustrated in Figure 1.3.

Figure 1.3: Diffraction within a photonic crystal.

For a DBR placed in air, equation. 1.16 becomes

$$\sin \theta_t = \frac{\sin \theta}{n_{eff}} \quad (1.17)$$

where θ and θ_t are the angle of incident and transmitted light. Using this relation, it is possible to define $\cos \theta_t$ as

$$\cos \theta_t = \sqrt{1 - \sin^2 \theta_t} = \sqrt{1 - \frac{\sin^2 \theta}{n_{eff}^2}} = \frac{1}{n_{eff}} \sqrt{n_{eff}^2 - \sin^2 \theta}. \quad (1.18)$$

In Figure 1.3, the difference between the optical path of the two beams can be expressed as

$$m\lambda = 2(n_{eff}BO' - CO). \quad (1.19)$$

Where BO' and CO can be calculated by simple geometrical considerations

$$BO' = \frac{D}{\cos \theta_t} = \frac{Dn_{eff}}{\sqrt{n_{eff}^2 - \sin^2 \theta}} \quad (1.20)$$

$$CO = BO \sin \theta = BO' \sin \theta \sin \theta_t = \frac{Dn_{eff}}{\sqrt{n_{eff}^2 - \sin^2 \theta}} \frac{\sin \theta}{n_{eff}} = \frac{D \sin^2 \theta}{\sqrt{n_{eff}^2 - \sin^2 \theta}} \quad (1.21)$$

Combining the equations 1.18 and 1.19 in 1.20 we find the Bragg-Snell's law that describes the stop band position (λ_b) as a function of the periodicity, the effective refractive index and the angle of incidence of light.

$$m\lambda_b = 2D \sqrt{n_{eff}^2 - \sin^2 \theta}. \quad (1.22)$$

1.3.3. The Stop-Band Properties

Before introducing the stop-band properties, it is useful to provide some definitions. Considering a DBR as a surface laying on the XY plane and the normal incidence as the z direction, the light polarization P (or transverse magnetic, TM) is defined when the electric field oscillates perpendicularly to the plane of incidence of the DBR and polarization S (or transverse electric, TE) when the electric field is parallel to the DBR plane (Figure 1.4).

Figure 1.4: Scheme of light polarization and tilting angle.

1.3.3.1. Light Polarization and Angular Dispersion

To explain the effect of light polarization on the stop-band it is useful to start analyzing the reflection of a single interface between air and an isotropic semi-infinite dielectric medium. The surface reflectivity for polarization S (R_s) and P (R_p) is described by the Fresnel's equations for the two light polarizations:

$$R_s = \left[\frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right]^2 \quad (1.23)$$

$$R_p = \left[\frac{n_1 \cos \theta_t - n_2 \cos \theta_i}{n_1 \cos \theta_t + n_2 \cos \theta_i} \right]^2. \quad (1.24)$$

The angular dispersion of R_s and R_p is shown in Figure 1.5.

Figure 1.5: Angular dispersion of the reflectance intensity at an isotropic interface for light polarizations S (blue line), P (green line), and for unpolarized light (red line).

In Figure 1.5, for $\theta < 10^\circ$, the reflectance intensity is approximately constant. At higher angles, for S polarized light, the reflectance increases with θ while, for P polarization it decreases to zero at the so called Brewster's angle (θ_B), and then increases again. The Brewster's angle, can be derived from Equation 1.23

$$\theta_B = \tan^{-1} \frac{n_h}{n_l}. \quad (1.25)$$

Applying the Fresnel's equation to a DBR, a reduction of the stop-band intensity at θ_B for polarization P is expected. Conversely, for polarization S the stop-band will be continuous in the range $0^\circ \leq \theta < 90^\circ$. Figure 1.6 reports the calculated angular resolved reflectance spectra for a cellulose acetate-polystyrene DBR. The spectra are illustrated as contour-plots, where the intensity is reported as a color scale. As predicted by equation 1.22, increasing θ , the spectral position of the stop-band (red tones) blue shifts in all the maps. For what concerns its intensity

and width, for polarization S, one can notice an increase with the angle of incidence until $\theta = 90^\circ$, where both the stop-band and the background reach the unitary value (Figure 1.6 a). On the contrary, for polarization P, the band intensity and width decrease to zero approaching θ_B and then increases again (Figure 1.6 b). When unpolarized light hit the sample, the spectral response is the average between the two polarization (Figure 1.6 c).

Figure 1.6: Angle resolved reflectance spectra for a polystyrene-cellulose acetate DBR. a) S polarization, b) P polarization, c) unpolarized light.

The strong angular dispersion of the stop-band spectral position, can be exploited for the light emission control, when tuning is required.³¹ On the other hand, in lighting applications, when steady enhancement or suppression of a single color is required, the stop-band angular dispersion may represent an issue.

1.3.3.2. Dielectric Contrast and Number of Periods

To understand how the dielectric constant affects a wave propagating into a periodic potential, it is useful to use again the analogy with semiconductors starting from the Kronig-Penney model, which considers the electron as wave propagating in mono-dimensional periodic potential subjected to a rectangular potential barrier with height V_0 , thickness b and periodicity a ,³⁵ Figure 1.7.

Figure 1.7: Rectangular potential barriers to electron propagations in a mono-dimensional periodic potential.

For photons propagating in a dielectric periodic potential given by media having different refractive index, the model can be expressed as:³⁶

$$\cos(kD) = \cos(k_1 d_1) \cos(k_2 d_2) - \frac{1}{2} \frac{n_1 + n_2}{n_1 n_2} \sin(k_1 d_1) \sin(k_2 d_2). \quad (1.26)$$

Along with the dispersion relations in the single layers $k_1 = n_1 \omega / c$ and $k_2 = n_2 \omega / c$, Equation 1.26 defines the dispersion relation for the propagation of light in the multilayer.

The Kronig-Penney model, whose graphical solution is reported in Figure 1.8 for normal incidence, implies the formation of stop bands in the dispersion relation for $|\cos(kd)| > 1$.

Figure 1.8: Dispersion relation for a photon propagating in a DBR.

Equation 1.26 can be solved, with some approximations, for a DBR in $\lambda/4$ conditions ($k_1 d_1 = k_2 d_2 = \pi/2$) for stop-bands centred at ω_0

$$\omega_0 = \frac{\pi c}{2} \frac{1}{n_1 d_1} = \frac{\pi c}{2} \frac{1}{n_2 d_2}. \quad (1.27)$$

In the $\lambda/4$ conditions, Eq. 1.26 becomes

$$\cos(kD) = -\frac{1}{2} \frac{n_1 + n_2}{n_1 n_2}. \quad (1.28)$$

Equation 1.28 does not admit real solution for $n_1 \neq n_2$. It is possible to impose a complex solution introducing an energy loss ($kD = \pi + ik$)

$$\cos(\pi + ik) = -\cos(ik) = \frac{1}{2} \frac{n_1 + n_2}{n_1 n_2} = \frac{1}{2} (e^\chi + e^{-\chi}) \quad (1.29)$$

where

$$e^\chi = \frac{n_2}{n_1} \quad (1.30)$$

And combining Eq. 1.27 and 1.30 we obtain

$$\omega_0 = \frac{c}{D} (\pi + i \ln e^\chi). \quad (1.31)$$

Which describes the radiation as a totally reflected wave, with a component decreasing with exponential attenuation along the z direction. When the dielectric contrast within the DBR is low ($\Delta n \ll n$), the extinction length (l) is approximated to

$$\frac{l}{D} = \frac{n}{\Delta n}, \quad (1.32)$$

which implies that light cannot propagate within a DBR with infinite dielectric contrast. From Equation 1.32 the analytical expression of the normal incidence transmittance for a DBR with number of periods N at the stop band wavelength can also be derivate:

$$T \propto e^{-ikD} \approx \left(\frac{n_1}{n_2} \right)^{2N} \quad (1.33)$$

Being $R+T=1$ for non-absorbing media:

$$R \propto 1 - 4 \left(\frac{n_1}{n_2} \right)^{2N}. \quad (1.34)$$

For angle of incidence $\theta \neq 0$, equation 1.34 assumes the forms:

$$R_p = 1 - 4n_s \cos \theta \left(\frac{n_1 \cos \theta_1}{n_2 \cos \theta_2} \right)^{2N} \quad (1.35)$$

$$R_s = 1 - 4n_s \cos \theta \left(\frac{n_1 \cos \theta_2}{n_2 \cos \theta_1} \right)^{2N} \quad (1.36)$$

for respectively P and S polarization.

From Equation 1.32, the width of stop-band can be defined as a function of the dielectric contrast (Δn) and of the average refractive index (n) in $\lambda/4$ condition

$$\frac{\Delta\omega}{\omega_0} = \frac{4 |n_2 - n_1|}{\pi (n_2 + n_1)} \approx \frac{2 \Delta n}{\pi n} \quad (1.37)$$

Equation 1.34 shows that the reflectivity value increase with the dielectric contrast and with the total number of layers in the DBR. It is then possible to achieve total reflection also with relatively low dielectric contrast by increasing N . In this regards, one of the main advantages of polymer structures is the possibility to equal the reflectance of inorganic DBRs (e.g. $SiO_2 - TiO_2$) with simpler fabrication processes. Figure 1.9 shows relation between reflectance intensity and N for a polymer DBR made by cellulose acetate ($n_{CA} \sim 1.46$) and

poly (N-vinylcarbazole) ($n_{PVK} \sim 1.68$). It is possible to see that the reflectance intensity at the stop band wavelength approaches 1 for $N=25$.

Figure 1.9: Relation between the stop-band intensity and the number of layers calculated for a DBR made by cellulose acetate and poly (N-vinylcarbazole).

The requirements of relatively high dielectric contrast and mutual processability among polymers pose some constraints. For instance, then DBRs are manufactured by spin-coating or dip-coating of polymer solutions, the two polymer-solvent couple must be insoluble one in the other. Then, the necessity to have mutually processable couples of polymers with relatively high dielectric contrast strongly limits the amount of available materials. To better explain this issue, Figure 1.10 reports the calculated spectra for four DBRs made of cellulose acetate and four co-processable polymers. As shown in the spectra, coupling cellulose acetate and poly (methyl methacrylate) (blue line) allows a small dielectric contrast resulting in stop-bands with reflectance intensity and width comparable with the interference pattern. In the same Figure, the same periodicity and number of periods is maintained, but the dielectric contrast is increased exchanging the layers of poly (methyl methacrylate) with layers of polystyrene (green line), poly (N-vinylpyrrolidone) (red line) and poly (N-vinylcarbazole) (black line). Comparing the spectra, one can notice that increasing the dielectric

contrast allows higher intensities and larger band-widths. Furthermore, the spectral position of the photonic peak red shifts as predicted by the Bragg-Snell's law.

Figure 1.10: Calculated reflectance spectra for DBRs made by cellulose acetate as a low index medium and four different polymers with increasing refractive index as high index media.

1.3.4. DBR Sensing

The effect of the DBR dielectric contrast on the stop-band intensity and width, described has important implication in sensing applications. Figure 1.11 shows the calculated spectra for a polymer (black line) and an inorganic (red line) DBR made of 15 +1 periods. The reflection peak assigned to the stop-band of the inorganic DBR is more intense and about 5 times broader than for the polymer lattice. This difference, which arises from the high dielectric contrasts typical of inorganic material pairs compared to those available for polymers affects strongly the sensing performances.

Figure 1.11: Calculated reflectance spectra of DBRs made by 15+1 periods of cellulose acetate-polystyrene (black line) and of $\text{TiO}_2\text{-SiO}_2$ (red line). The inset shows the multilayer architecture.

While high dielectric contrast is always desirable for light management applications,³³ it may hinder sensitivity and increase detection limit in sensing applications. Indeed, the interaction with analytes can induce large spectral variations of the narrow stop-bands typical of polymer DBRs. Conversely, the broad stop-bands of inorganic DBRs do not undergo large spectral changes. To illustrate the differences in the optical response of inorganic mesoporous and polymer DBRs, and the motivations which drove us to focus on the latter, it is first necessary to briefly explain the DBR sensing mechanism.

Sensing relies on the optical response generated by the variation of the DBR effective refractive index and periodicity, which can be induced by the intercalation of an analyte within the structure. The phenomena occurring in the DBR upon exposure to analyte vapors can be related to its spectral response by three simple equations. As shown in Paragraph 1.3.2, the Bragg Snell's law describes the spectral position of a DBR stop-band (λ_b) as a function of the lattice periodicity (D), its effective refractive index (n_{eff}) and the angle of incidence of light (θ):

$$m\lambda_b = 2D \sqrt{n_{eff}^2 \sin^2 \theta} \quad (1.22)$$

The variation of the dielectric contrast also affects the intensity of the reflectance peak as described by Eq. 1.34

$$R \propto 1 - 4 \left(\frac{n_1}{n_2} \right)^{2N}, \quad (1.34)$$

and the stop-band width

$$\frac{\Delta\omega}{\omega_0} = \frac{4}{\pi} \frac{|n_2 - n_1|}{n_2 + n_1} \approx \frac{2}{\pi} \frac{\Delta n}{n}. \quad (1.37)$$

These simple equations allow describing the differences in the optical behavior of DBR sensors during the penetration of an analyte.

The optical responses calculated for the penetration of an analyte in an inorganic porous DBR and in a polymer DBR are compared in Figure 1.12. The spectrum of the inorganic structure is modelled for 4+1 periods of two media with comparable thickness and volumetric porosity (black line of Figure 1.12 a). The spectrum shows a broad stop-band induced by the high dielectric contrast among the DBR media (Eq. 1.37). The peak ranges from 430 nm to 790 nm with intensity close to the unit in the entire range. When a vapour analyte penetrates within the porous DBR and condensates, the stop-band red-shifts, according to the analyte refractive index n_a in the liquid phase (blue line of Figure 1.12 a).^{15, 19, 22, 37-42} Indeed, the rigidity of the inorganic layers does not allow any variation of D . Moreover, being $n_a > n_{air}$, the effective refractive index can only increase, with magnitude depending on the analyte concentration within the lattice (See

Paragraph 1.3.3). Although the optical response of these systems is very straightforward and easy to interpret, the broad stop-band often makes evaluation of the overall spectral response difficult.⁴³

In the case of polymer DBRs, thanks to the lower dielectric contrast and sharp stop-bands, the response to analytes is much stronger. Moreover, the polymers ease of swelling (variation of D) further enhances the optical response. The black line of Figure 1.12 b shows the calculated reflectance spectrum for 10+1 periods of two polymers with comparable thicknesses and with refractive indexes $n_H = 1.68$ and $n_L = 1.46$. The spectrum shows a maximum of reflectance at about 550 nm, with band width of ~100 nm. When an analyte penetrates within the multilayer, it induces both thickness and refractive index variation. The final position and intensity of the stop-band is then defined by the combined variation of n_{eff} and D , as described by Equations 1.22 and 1.34. For sake of simplicity, we consider the variation of refractive index and thickness of a single medium at a time. Figure 1.12 b shows a schematic of the processes occurring after the intercalation of a vapour analyte with liquid phase refractive index $n_a = 1.5$ within the DBR. When one of the polymer layer is swollen, D increases inducing a red shift of the stop-band (green and red lines in Figure 1.12 b). Moreover, if the analyte induces a decrease of the dielectric contrast, the intensity of the stop-band will decrease according to the analyte concentration (green line), and vice versa (red line).

Despite the disadvantage of high dielectric contrast, mesoporous DBR sensors have been widely reported in literature, mainly due to the high porosity that facilitates analyte penetration. On the other hand, the fabrication of these structures is very time consuming and the response is often hardly detectable. Considering these limitations, polymer DBRs seem a viable solution to achieve better sensing performances at lower costs. The issues related to the low permeability of these structures, can be reduced embedding permeable polymer layers within the DBR structure. This thesis proposes two different approaches to achieve this goal. The first consists in the implementation of highly permeable

nanocomposite layers within the DBR. For this purpose, ZnO nanoparticles were dispersed into polystyrene matrix to introduce free volumes into the polymer thus allowing vapor permeation.

a) Porous inorganic DBR

b) Amorphous polymer DBR

Figure 1.12: Schematic of the optical response induced by the analyte penetration in a) inorganic mesoporous and b) amorphous polymer DBRs.

The new nanocomposite permits high sensitivity but does not show full selectivity among VOC. To discriminate among vapors with similar chemical structure and properties, poly(p-phenylene oxide) (PPO) was implemented as active medium into the sensing platform. PPO is indeed able to intake large amount of analyte and to crystallize into different phases with dissimilar optical properties, which depend on the analyte. This behavior has been widely reported

by the group of Prof. G. Guerra.⁴⁴⁻⁴⁸ They showed that the sorption of organic molecules can induce the formation of clathrate co-crystals where the guest molecules are intercalated within the polymer chains. As an example, Figure 1.13 a shows the X-ray diffraction pattern for bulk PPO after intercalation of decaline (A'), α -pinene (B'), benzene (C') and carbon tetrachloride (D'). Notwithstanding the solvent-induced crystalline structures of PPO have not been determined for all the solvents reported by the authors (See Ref.⁴⁸ for peak indexing in the case of α -pinene intercalation) such data allow the determination of the polymer crystallinity by subtracting the scattering of amorphous phase from the diffraction pattern even without peak indexing.⁴⁹ Figure 1.13 b, reports instead the clathrate PPO- α -pinene co-crystalline lattice.

Figure 1.13: X-ray diffraction patterns of PPO co-crystals fabricated by intercalation of decaline (A'), α -pinene (B'), benzene (C') and carbon tetrachloride (D').⁵⁰ PPO- α -pinene co-crystalline lattice.⁴⁸

1.4. Outcomes

This Thesis demonstrates label-free selective polymer DBR sensors, which are sensitive to VOC vapors. Sensitivity is achieved by inclusion of thin films of

poly(p-phenylene oxide) and polystyrene-ZnO nanocomposite as active sensing regions in standard polymer DBRs. The use of polymers also allows strong spectral responses, easily interpretable even via the naked eye.

The nanocomposite structures were made by alternate layers of cellulose acetate and polystyrene matrices loaded with ZnO nanoparticles. The nanoparticles introduce free-volume in the DBR and increases its permeability allowing sensitivity to VOC vapors. The new sensors show different optical behavior to environments rich in benzene, ortho dichlorobenzene and carbon tetrachloride but cannot distinguish among molecules with very similar structures such as benzene and toluene. The limited selectivity of the nanocomposite structure was overcome using poly(p-phenylene oxide) as active sensing medium allowing sensitivity and full selectivity among toluene, benzene, carbon tetrachloride and ortho dichlorobenzene.

These results promise new concept devices for the fast and selective detection of vapors, which now requires collection of large amount of air and laboratory characterizations. Moreover, the capability to assess the DBR optical response to polluted environment by naked eye, will allow un-trained operator to evaluate endangering atmosphere without the use of any equipment. This capability will also simplify the detection of pollutants in remote areas such as the ocean surface, often affected by oil spills, without necessity of additional instrumentation.

1.5. References

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Chapter 2

Literature Review

This Chapter reviews established and recent technologies for the detection of volatile organic compound vapors focusing on advantages and limitations in term of sensitivity, selectivity, ease of fabrication, and of signal transduction. The first Paragraph reports on established methodologies for quantitative and qualitative analyses, used respectively in industrial plants and when the pollution source is unknown. The second and third Paragraphs review new concept devices based on chemically labelled colorimetric targets and distributed Bragg reflector sensors.

2.1. Established Technologies for VOC Detection

VOC detection and monitoring are usually ruled by national regulations, which vary country by country. In general, quantitative analyses are performed using portable detectors, while qualitative measurements are more complicated. In industrial areas, where pollutant species and sources are usually known, detection of small concentrations of pollutants is necessary to avoid excessive and prolonged exposures. On the other hand, in urban and rural environments, the large amount of activities that may release these compounds makes the identification of pollutants of primary importance to evaluate the risks. Consequently, the figure of merit of VOC detectors may vary strongly. While in industrial area the main requirement is sensitivity and low detection limit, in cities and rural areas, the identification of the pollutant, and thus the selectivity of the detection system is most critical. The next Paragraphs will review the established technologies used to monitor air quality, highlighting the figures of merit of detection systems. Then, recent literature on colorimetric and photonic crystal sensors will be described.

2.1.1. Sensors for Quantitative Analyses

Among the most diffuse portable detectors are colorimetric indicator tubes, metal oxide sensors, and portable infra-red point sensors, which will be described in this section, as well as photoionization detectors which will be introduced in the next Paragraph.

Metal Oxide Sensors are based on the change of conductance of metal thin films induced by the formation of oxygen vacancies by reaction with the analyte. The working principle of these systems relies on a catalyzed red-ox reaction between the VOC, that is oxidized, and a metal oxide, which is reduced (Figure 2.1). In non-reducing environment, the electrons in the oxide are attracted toward oxygen, which is adsorbed on the surface sensor. In presence of a reducing gas,

the oxygen reacts, and its surface density decreases. This process releases electrons and reduces the resistance of the circuit.¹ Although these sensors have sensitivity down to few parts per billion, the lack of selectivity and the presence of ozone and water can generate false readings.^{2,3}

Figure 2.1: Schematic of a metal oxide detector for VOC vapors analysis.

Colorimetric indicator tubes are glass tubes containing specific chemical targets for the analytes. Figure 2.2 shows a commercial system where a volumetric hand pump (a) is directly connected to the glass tubes containing the chemical target (b). The variation of the target color is compared with a database to define the analyte concentrations. These tests can detect concentrations ranging from few parts per million to few percent, but accuracy is generally low.⁴

Figure 2.2: Commercial colorimetric reaction tube detector: a) volumetric hand-pump and b) colorimetric glass tubes for different analytes.⁵

Portable infrared point sensors use vibrational infrared spectroscopy to detect hydrocarbons. These sensors measure two wavelengths: a measuring wavelength

corresponding to the analyte absorption, and a reference wavelength detuned from the absorption. The working principle is illustrated in Figure 2.3. When the analyte is placed in the optical path of the measuring beam, radiation is absorbed and the analyte concentration is evaluated by comparison between the relative intensity of the measuring and reference beams.⁶ These systems can be used for both *in-situ* and remote detection and possess high sensitivity, but the presence of different analytes with absorption in the same spectral range may induce false readings.

Figure 2.3: Schematic of infrared point detector components.

2.1.2. Sensors for Qualitative Analyses

Portable detectors do not allow pollutant identification, so laboratory analyses are necessary when the source is unknown. VOC discrimination requires the collection of large amount of air and the separation of the different pollutants before measurements can be performed. The procedure consists of three main steps: sampling, separation and detection.

- **Sampling:** air is usually sampled over a long period in an area selected considering meteorological data and distance from the source. The pollutants can be collected in pressurized canisters⁷ or concentrated by membrane based enrichment techniques⁸⁻¹⁰ and, at times, further concentrated by solvent extraction or cryogenic methods.¹¹⁻¹⁵
- **Separation:** once sampled and concentrated, the analytes are separated via gas chromatography: the sample is carried by an inert gas (the mobile phase)

through a column containing a stationary phase. The latter interacts with the analytes causing each compound to be eluted with different time.¹⁶ Since elution times are not unique, the sample often needs to be split into two columns with different selectivity.¹⁷

- **Detection:** for qualitative analyses, two detectors are usually connected to the chromatographic column in series or parallel configuration to obtain better compositional information.¹⁸ For systems connected in series, the first module must perform non-disruptive analyses, posing some constraint to the detector choice. Parallel detectors can instead be disruptive, but splitting the sample induces loss of sensitivity.¹⁹

The most commonly used method for VOC assessment is mass spectrometry. Mass spectrometry relies on fragmentation and separation of the analytes depending on their mass to charge ratio. In this detector, shown in Figure 2.4, the gas flow from the chromatography column reaches the fragmentation chamber. Here an electron beam ionizes and fragments the molecules. The fragments are then accelerated and separated depending on their mass and charge by magnetic lenses or dipoles, generating a unique spectrum. The data are then compared with a library to identify the analytes.²⁰

Figure 2.4: Schematic illustration of a mass spectroscopy detector.

Other commonly used systems are photoionization detectors. These detectors are selective and non-destructive, and can be used for the characterization of

aromatic substances with sensitivity of picograms. In these modules, the VOC are directly injected in to the detector chamber from the chromatographic column (Figure 2.5). A krypton lamp emits photons at 112.6 nm and 123.6 nm able to ionize molecules with ionization potential smaller than 10 eV.²¹ The new species are then collected from two electrodes and generate a current. In this detection system, sensitivity is affected by the chemical structure of the analytes including number of carbons, functional groups and their position.

The non-destructive nature of the measurement derives from the low ionization efficiency of the analytes (e.g. 0.1% for benzene), which allows the major part of the sample to reach the second detector. The main issue related to this system is the reduction of transmission of the UV window, which is often affected by accumulation of stationary phase residual carried with the gas flow from the chromatography column. Consequently, the detector needs frequent calibration and maintenance.

Figure 2.5: Schematic representation of a photoionization detector.

The organic species can be ionized also by an air/hydrogen flame in *flame ionization detectors*. Here, the detector reads a positive signal due to the presence of carbon in the flame.²¹ As shown in Figure 2.6, the stream from the chromatographic column is mixed with a hydrogen flow and ignited in the detector chamber. When the analytes contact the flame, the detector reads a signal due to the presence of carbon. This is considered a destructive quantitative

system. The response is proportional to the number of carbon introduced into the flame with a linear dynamic range about five order of magnitude and sensitivity of $\sim 0.5 \mu\text{g/ml}$.²¹ This detector is subjected to contamination and obstruction in analyses of VOC with relatively high molecular weight, thus requiring frequent calibration.

Figure 2.6: Schematic illustration of a flame ionization detector.

2.2. Colorimetric Technologies for Qualitative VOC Monitoring

New sensors relying on the variation of photoluminescence²²⁻²⁷ and color²⁸⁻³⁶ based on the interaction between the analytes and chemical targets are increasingly researched to develop devices that require simpler instrumentation than current standard techniques. Usually these detectors exploit arrays of pixels of chemical targets with different reactivity. Different interactions between the pixels and the analyte generate a characteristic matrix of colors that allows identification of the analyte via chemiometric analysis. The labels can exploit polarity, acidity or red-ox reactions.³⁷ Chemical receptors can indeed be metalloporphirines,^{28, 38} reducing agents,³⁹ or conjugated systems such as

functionalized polyacetylenes.^{22, 33, 34, 40} Some devices can contain a mixture of labels to achieve broader selectivity.^{41, 42}

The main advantages of colorimetric detectors are the low cost and simplicity. On the other hand, the response transduction relies on the color variation of large matrices, which requires chemiometric analysis and comparison with reference libraries. Furthermore, at time the response is not detectable by spectroscopy and requires complicated colorimetric analyses of array of labels; the response of a typical colorimetric device is reported in Figure 2.7.³⁷ Here, an array of 36 chemical labels containing pH indicators, solvatochromic dyes, and metalloporphyrins shows different colorimetric changes to VOC vapors (Figure 2.7 a). The response is analyzed by a camera to extract a color difference map (Figure 2.7 b). The map is then used to create a library of responses suitable for VOC identification (Figure 2.7 c). A clear disadvantage of such systems is the complicated colorimetric analysis necessary to determine VOC concentrations.

Figure 2.7: Chemically labelled colorimetric array sensor for VOC identification.³⁷

2.3. Photonic Crystal Sensors

As described in Paragraph 1.3.4, photonic crystal sensing relies on the penetration of an analyte within the lattice and the consequent variation of its refractive index and periodicity. Consequently, highly permeable porous lattices such as opals,^{37, 43, 44} colloidal crystals,^{45, 46} porous inorganic⁴⁷⁻⁵⁰ and hybrid^{51, 52} DBRs are highly sensitive to both liquid and gas analytes. On the other hand, these structures suffer from long fabrication procedure, and can hardly achieve selectivity without chemical labelling. These issues can be addressed using polymer DBRs. These structures can be grown by simple and fast techniques such as co-polymers self-assembly,⁵³ dip-coating⁵⁴ and spin-coating,⁵⁵ and even at the industrial scale by coextrusion.⁵⁶ Moreover, their narrow stop-bands allow strong spectral responses, further amplified by the ease of swelling of the polymer media. Thanks to these factors, polymer DBR sensors demonstrate high sensitivity and response, easily detectable by the naked eye in the case of analytes in the liquid phase.⁵⁷⁻⁶⁴ However, the low permeability to gas and vapors of amorphous polymer and the lack of selectivity hinders their use for the detection of vapors: for this reason only few vapor sensitive polymer DBRs have been reported so far. The next Paragraphs compare porous and polymer sensors in terms of sensibility, selectivity, ease of fabrication and of signal transduction.

2.3.1. Mesoporous Inorganic DBR Sensors

Despite processing issues and low spectral response (See also Paragraph 1.3.4), inorganic mesoporous DBRs were proven suitable for VOC discrimination.

In 2010, G. A. Ozin and co-workers showed a DBR made of layers of SiO_2 and TiO_2 fabricated by spin-coating and thermal annealing of the respective colloidal solutions. The DBR was able to discriminate among aliphatic molecules with very similar structure.⁶⁵ To achieve selectivity, the DBR was divided into 9 pixels whose were functionalized with different silanes to gather diverse hydrophobicity

to the surface (Figure 2.8 a). The interaction between the functionalized pixels and the analytes offered a modest optical response, impossible to detect by standard spectroscopic techniques. Consequently, the pixels were analyzed via a *Color Imagery Analysis*. This method is based on the transduction of the color variation of any pixel in a RGB pattern. The analysis of any sensing device produces a matrix of 27 elements (3 colors for 9 pixels). The matrix is analyzed via chemiometric analyses (Figure 2.8 b) to generate a library of responses. The sensor is capable of distinguishing among various molecules with very similar structure and properties, such as linear hydrocarbon and alcohol with comparable molecular weight.

Figure 2.8: a) Pixilation and functionalization of selective TiO₂-SiO₂ DBR. b) Transduction of the pixel response into RGB code.⁶⁵

The complicated data analyses related to chemically labelled sensors can be extremely simplified when the device shows an intrinsic response to the analyte. Label-free discrimination by mesoporous DBRs was demonstrated by B. V. Lotsch and co-workers using size selective zeolite/ TiO_2 DBRs.⁴⁸ The DBRs were fabricated by alternate spin-coating and thermal annealing of TiO_2 and zeolite nanoparticles dispersion. Figure 2.9 a shows a scanning electron microscope cross sectional image of a sample where the small TiO_2 nanoparticles appear as bright layers alternated to zeolite darker spheres. The DBR shows spectral shift of the stop-band position depending on analyte species and concentration induced by the size selective zeolite layers (Figure 2.9 b).

Figure 2.9: a) Zeolite/ TiO_2 DBR cross sectional scanning electron microscopy micrograph, and b) spectral response to alcohol vapors.⁴⁸

Although such devices provide label-free sensitivity, the fabrication of inorganic systems is hard to scale-up and time demanding due to the thermal annealing process necessary after the deposition of each layer to provide mechanical stability.^{48, 65, 66}

2.3.2. Hybrid Polymer-Inorganic DBR Sensors

In 2016, Lazarova et. al. demonstrated hybrid organic-inorganic permeable devices made by alternated layers of poly (methyl methacrylate) and porous

layers of V_2O_5 .⁶⁷ The sensors were fabricated by alternated spin-coating and thermal annealing of a vanadium sol and a polymer solution. Figure 2.10 a shows the spectral response of the DBR to vapor of chloroform. The relatively low dielectric contrast between the polymer and the porous V_2O_5 allows a narrow stop-band undergoing significant spectral variation upon chloroform vapor exposure. Lazarova also compares the response of DBRs made by porous and compact inorganic layers (Figure 2.10 b-d) and demonstrates that the porosity of the thin inorganic layer allows penetration of the analyte within the DBR and thus stronger response induced by a swelling of the polymer films by 5%.

Figure 2.10: a) Reflectance spectra of V_2O_5 - Poly (methyl methacrylate) DBR during chloroform exposure. Picture of the sample before (b) and after (c) Chloroform exposure. c) Comparison between the responses of DBR made with porous (blue) and compact (red) V_2O_5 .⁶⁷

2.3.3. Polymer DBR Sensors

As mentioned above, due to lack of sensitivity, only few DBR vapor sensors have been reported so far. In 2003, Convertino et al. showed a DBR made of alternated layers of bare and gold doped fluorinated polymers fabricated by chemical vapors deposition.^{68, 69} After 100 minutes of exposure to acetone vapors, the DBR layers swollen (Figure 2.11 a) inducing a red shift of the stop-band from ~ 1600 nm to ~ 1700 nm (Figure 2.11 b).

Figure 2.11: a) Fluorinated polymer DBR swelling after acetone vapors exposure and b) optical (left panel) and temporal (right panel) response to the vapors.⁶⁸

In 2006 Mönch et al. reported a multilayer grown by spin coating of monomeric precursors of poly (methyl methacrylate) and polystyrene, and *in-situ* polymerization by ultraviolet curing, which achieved good sensitivity to acetone

and toluene vapors.⁷⁰ In Figure 2.12 a, the DBR optical response to acetone shows a red shift of the stop-band from 550 nm to 1100 nm. Long time-scale response to toluene and the reversibility of the system are reported in Figure 2.12 b. The crosslinked polymers allow the DBR stop-band to return to its initial position after the exposure within few hours. On the other hand, the system requires more than 100 h to reach the equilibrium and undergo the 550 nm red-shift.

Figure 2.12: Behavior of cross-linked poly (methyl methacrylate)-polystyrene DBR during vapor exposure. a) Optical response to acetone, and b) temporal response and reversibility to toluene.⁷⁰

Summarizing, while permeable inorganic DBRs have been demonstrated capable of vapor sensitivity and label-free selectivity, the time consuming fabrication techniques and the often complicated signal transduction hinder their use for extensive monitoring of vapor pollution. Hybrid structures can enhance the

spectral response coupling inorganic porous permeable media with swellable polymer thin films. On the other hand, also these systems require long thermal annealing to achieve mechanical stability. The low permeability of polymer DBR limited their use as vapor sensors. Indeed, only few systems capable of vapor detection have been reported so far. Moreover, all the polymer sensor reported within this Paragraph are fabricated by costly or time consuming techniques such as chemical vapor deposition and *in-situ* polymerization. Consequently, the possibility to fabricate permeable polymer DBR sensors with sensitive and label-free selective response by fast and low-cost method like spin-coating or co-extrusion is attractive to reduce costs and to allow extensive monitoring of air pollutants.

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Chapter 3

Experimental Methods

This Chapter reports the experimental methods employed within the project. The first Paragraph summarizes the approaches used to achieve sensitive and selective distributed Bragg Reflectors sensors. Materials, fabrication methods, characterizations techniques and optical modelling are then explained in details.

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3.1. Materials and Methods for Label-Free Selective Vapor Sensors

The previous Chapter reviews common technologies for selective detection of VOC. While standard methodologies require complicated and time consuming analyses, colorimetric technologies need complicated signal transduction. Notwithstanding the low permeability to vapors and the lack of selectivity so far, the low cost, ease of manufacturing, and strong spectral response of polymer DBRs make these structures promising for a new generation of VOC detectors capable of label-free selectivity detectable by the naked eye, that is without the need of a spectrophotometer. In this project, new polymer media able to overcome both permeability and selectivity issues are demonstrated. The new sensors were developed starting from a prototype DBR made by alternated layers of polystyrene and cellulose acetate which shows negligible optical response to VOC vapors. To achieve this, a new optical nanocomposite was engineered to introduce free volume within the polystyrene layers, and to increase the overall DBR permeability. The nanocomposite was realized by doping the polymer with ZnO nanoparticles (NPs). The implementation of the nanocomposite into the prototype DBR allows high sensitivity and selectivity among VOC with very dissimilar structure, but not among homologues such as benzene and toluene. The capability of poly (p-phenilenoxide) (PPO) to absorb high amount of guest molecules and to form co-crystalline phases whose optical properties depend on the absorbed analyte¹⁻⁵ was used to improve the selectivity of the systems while maintaining the permeability to vapor analytes.

3.2. Fabrication of Polymer Thin Films and DBRs

3.2.1. Synthesis of ZnO Nanoparticles

To fabricate the nanocomposite DBRs, ZnO nanoparticles were synthesized via a solvothermal route and their surface was modified to favor their dispersion in

the non-polar polystyrene matrix. The modified nanoparticles were then loaded in polystyrene solutions used to grow thin films and DBRs by spin coating. This Paragraph describes the procedure used for the fabrication and the techniques employed for the characterization of the nanofiller and nanocomposite thin films.

ZnO nanoparticles were synthesized starting from zinc acetate dihydrate and potassium hydroxide. In a typical process, 0.07 mol of zinc acetate are dissolved in methanol and heated at 63 °C under sonication. Then, 0.14 mol of potassium hydroxide are dissolved in the same solvent and slowly added to the first solution. After 3 hours of reaction, the particles are purified by five cycles of decantation and washing with methanol, and finally dried.

ZnO formation is attributed to the acetate hydrolyzation initiated by the alcoholic solvent (Figure 3.1, reactions 1 and 2) and a further esterification between the hydrolyzed acetate molecules (reaction 3). The esterification produces ZnO and water by condensation.^{6, 7}

Figure 3.1: Mechanism of ZnO nanoparticles formation.

To avoid ZnO particles aggregation, responsible for light scattering in the non-polar polystyrene, methoxy (dimethyl) octadecylsilane (DMMOS) was grafted on their surface. To achieve the grafting, 10 g of nanoparticles were dispersed in 30 ml of methanol and sonicated. Then, 70 ml of dichloromethane containing 2.5 g of DMMOS were added to the dispersion. The overall dispersion was then sonicated until complete evaporation and desiccated in a vacuum at 40 °C for 2 h. The reaction between the surface and the adsorbed DMMOS was run at 135°C under nitrogen flux for 2 h.⁸

The graft reaction between the surface and the adsorbed DMMOS consists in the formation of a covalent bond between the only DMMOS functional group (-OCH₃) and the ZnO nanoparticles hydroxyl groups (Figure 3.2).

Figure 3.2: Mechanism of ZnO nanoparticles grafting.

3.2.2. Fabrication of Nanocomposite Thin Films and DBRs

To fabricate the nanocomposite thin films, the grafted ZnO nanoparticles were dispersed into toluene solutions of polystyrene (Sigma Aldrich, MW = 200000)

and stirred for more than 36 h at room temperature. The thin films were grown by dynamic spin coating of colloidal solutions with polystyrene concentration ranging from 3 to 5 % (w/v) and nanoparticle load of 1%, 2.5% and 5% (v/v_{PS}).

These films were then alternated to layer of cellulose acetate (Sigma Aldrich, MW = 61 000) dissolved in diacetone alcohol. The polymer concentrations ranged from 3 to 5 % (w/v) and the rotation speed during the deposition was kept at about 100 rps.

3.2.3. Fabrication of PPO Thin Films and DBRs

Poly(p-phenylene oxide) (Sigma Aldrich, Mw=100,000) thin films in both amorphous and co-crystalline phases were fabricated by dynamic spin coating from solution of toluene and carbon tetrachloride.

Thanks to better optical quality and absence of light scattering, the amorphous polymer was implemented in DBR sensors. DBRs were fabricated by dynamic spin coating of alternated layer of the PPO-toluene solution and cellulose acetate dissolved in diacetone alcohol. The concentration for the two polymers ranges between 3% and 12.5 % (w/v), while the spin speed ranges from 15 to 100 rps.

3.3. Characterization

3.3.1. Nanocomposite Surface Topography and Nanoparticles Size

Loading nanoparticles into a polymer matrix can potentially lead to scattering phenomena caused by large particle sizes or formation of aggregates. In turn, light scattering strongly affects the optical quality of the multilayers. To assess the nanoparticles size and the presence of aggregates, both the nanoparticle and the nanocomposite surface were investigated by scanning electron microscopy (SEM). The measurements were performed with a field emission microscope Jeol JSM6700F. Secondary electron micrograph were collected using an acceleration

voltage ranging from 2.5 kV for the non-conductive polymer matrices to 10 kV for the nanoparticles. For the measurement, the nanocomposites solution containing grafted and bare ZnO nanoparticles were spun-cast on a p-type silicon wafer and analyzed without further treatments. The ZnO nanoparticles were drop-cast from methanol solutions on the same silicon substrate.

In a typical secondary electron, SEM analysis, an electron beams with energy ranging from 0.2 kV to 20 kV is focused by condenser lenses to the sample surface down to a spot size down to few nanometers. The primary electron beam interacts with the sample, where low-energy secondary electrons are ejected from the k -shell of the atoms and then collected to form an image with brightness depending on the surface topography. Compared to other SEM techniques, detection of secondary electrons allows measurement of thin samples with low conductivity. Indeed, charging effects can be compensated using low energetic primary electron beam. This is particularly advantageous for the imaging of semiconducting nanoparticles and polymer thin films. Indeed, the deposition of conductive metals or carbon layers necessary to avoid charging phenomena hinders dimensional estimations.⁹

The nanoparticles crystal size was manually measured from SEM micrographs and confirmed by powder X-ray diffraction analyses (XRD).¹⁰ For this purpose step scan powder diffraction patterns were collected with a D8 Advance Bruker in the 2θ range between 25° and 75° . The nanoparticles crystallite size was correlated to XRD diffraction peaks by the Debye-Scherrer equation¹¹

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3.1)$$

where D is the crystallite dimension, k is a constant and β is the full width at half maximum of the diffraction peak.

3.3.2. Thin Film Optical Constant

The optical constants of the new nanocomposite thin films were measured to confirm their optical quality and to determine the variation of the matrix refractive index induced by the nanofiller (See Paragraph 1.3.1). The data are also used as input in the DBRs modelling, therefore they were measured for all the polymers used in this project.

Spectroscopic ellipsometry was performed to determine the film refractive index and absorption coefficient¹² using a VASE ellipsometer by J.A. Woollam Co. Inc. and analyzed using the commercial software WVASE32®. Incidence angles ranging from 55° to 75° were used. Ellipsometry relies on the variation of polarization due to the reflection at an interface. In Figure 3.3 an incident beam linearly polarized undergoes amplitude and phase change upon the reflection at a plane interface.

Figure 3.3: Schematic of ellipsometric measurement used to determine the optical constants of polymer films.

The variation is analyzed by a second polarizer placed before the detector. Ellipsometry measures the complex reflectance ratio ρ of a system, which can be parametrized by the phase shift Δ and the amplitude ratio Ψ of the electric field upon reflection

$$\tilde{\rho} = \tan\psi e^{i\Delta} \quad (3.2)$$

Being $\rho = \rho(\tilde{n}, d, \lambda, \theta)$, regressive analysis based on the sample modelling allows retrieving the optical constants. The model predicts the Fresnel coefficients for the system, which describe each layer in term of their thickness and optical constants. The calculated values are fitted to the experimental data by regression.

3.3.3. Thin Film Thickness

Together with the refractive index, the film thicknesses are inputs for the modelling of the DBRs optical response. Measurements of the film thickness was not necessary for DBRs in $\lambda/4$ condition, where the thickness can be calculated by the spectral position of the stop-band (see Paragraph 1.3.2). For all the other samples, the film thicknesses were measured by light interferometry using a GBS smart WLI microscope with a 20x interference objective.¹³ The film thickness within the DBRs was calculated as the difference between the values for bilayers and monolayers spin-coated onto a glass substrate. This was necessary because the glass surface has diverse roughness and polarity than the polymer, thus affecting the spin-coating process and the final polymer thickness.

Interference microscopy relies on the interference signal achieved by separation and recombination of a reference and a measurement beam. The measurement beam travels to the sample surface, while the reference beam is reflected by a mirror (Figure 3.4). The topography of the samples modifies the optical path of the measurement beam generating an interference. Compared to contact methods, such as atomic force microscopy, interference imaging allows much faster measurements with comparable vertical resolution and significantly larger sampled areas.

Figure 3.4: Schematic of the interference microscope used for the determination of polymer film thicknesses.

Figure 3.5 reports the typical interference microscopy data retrieved for a thin film. The top panel shows the topographic map of a scratched cellulose acetate thin film associated to the thickness profile in the bottom panel.

Figure 3.5: a) Topographic map and b) thickness profile of a scratched cellulose acetate thin film.

3.3.4. Permeability Enhancement

The permeability of polystyrene matrices doped with the inorganic load was evaluated by pressurized helium permeation tests on freestanding nanocomposite and bare polystyrene thin films. In this analysis, helium is pressurized and permeated through a freestanding polymer film fabricated by drop-casting. Thin film permeability was measured with the home-made system shown in Figure 3.6. The apparatus consists of a sealed stainless-steel cylinder with a pipeline for gas flow. The sample is placed in the gas line with a rubber seal to avoid gas leakage. Helium pressure is applied on top of the sample and the permeating flow is measured after the sample. The applied pressure ranges from 180 Pa (~ 1.00099 ata), which corresponds to the lower analyte vapor pressure used during the sensing experiments, to 2000 Pa (1.197 ata). At higher pressures the thin samples would crack.

Figure 3.6: Thin film permeability measurement setup.

The flowmeter consists in a graduated glass tube connected to a rubber bulb containing a soap solution (Figure 3.7). Squeezing the bulb, the soap level is raised to form a meniscus (bubble) above the gas inlet. This meniscus, which has negligible weight and low friction, serves as a gastight piston. Once the gas flow enters the tube, the meniscus is timed over the known volume between the two marks. The flow rate is then calculated as the ratio between the volume and the traversing time of the meniscus. Modifying the diameter of the tube, and thus the

traversing volume, it is possible to measure flows ranging from 0.1 and 1000 cm s⁻¹, with error below $\pm 1\%$.¹⁴ The gas flow rate passing through the sample is then related to the permeability (PE) by:

$$PE = \frac{Ql}{\Delta PD} \quad (3.2)$$

where Q is the He molar flow, ΔP is the He pressure, l and D are the film thickness and the permeation area respectively.

Figure 3.7: Bubble flowmeter

3.3.5. Assessment of PPO Phase Transition

The different PPO phases were assessed by ellipsometric spectroscopy as described in Paragraph 3.3.2. and by infrared spectroscopy. Two different techniques were employed to allow vibrational spectroscopy without requiring

vacuum or controlled environment, which may affect the PPO crystalline phase. Because of its simplicity, attenuated total reflection (ATR) spectroscopy was used to measure as cast thin films. However, this technique relies on the contact between the sample and a crystal, which may affect the PPO nanoporous crystalline phase. Therefore, PPO films exposed to VOC vapors were measured by polarization modulation infrared absorption reflection spectroscopy (PM-IRRAS).

ATR was used to evaluate the PPO phase of thin film spun-cast from toluene and carbon tetrachloride solutions on cellulose acetate layers to reproduce the condition of deposition illustrated in the previous Paragraph. The technique measures the changes occurring in a beam totally reflected within a crystal contacting the sample. The infrared beam directed into the crystal undergoes total internal reflection creating an evanescent wave that extends few microns beyond its surface to a sample held in contact with it (Figure 3.8).

Figure 3.8: Scheme of ATR measurement.

PM-IRRAS allows to measure thin film without contacting the surface with the probe, and it is particularly useful for swollen DBR samples. PPO amorphous films fabricated by spin-coating at 80 rps of 3% wt toluene solutions onto gold surfaces were measured and then exposed for 30 minutes to saturated environments of toluene, benzene, ortho dichlorobenzene and carbon tetrachloride at room temperature before being further measured. The PM-IRRAS spectra were collected at incidence angle of 85° using a Bruker Tensor 27 FT-IR spectrometer coupled to a PMA50 external module equipped with a

linear KRS5 linear polarizer, a ZnSe 50 kHz photoelastic modulator (PEM, by HINDS), an optical filter (transmitting below 4000 cm^{-1}), a variable angle reflection accessory, and a narrow band MCT (mercury cadmium telluride) detector.

In a typical PM-IRRAS experiment, the sample is analyzed in reflection geometry under a grazing incidence for both P and S polarizations.¹⁵ According to Fresnel's equations, when a S polarized beam is reflected at a metal surface, its phase changes of $\sim 180^\circ$ resulting in a disruptive interference near the surface (Figure 3.9 b). Conversely, high phase shift for polarization P occurs only at angle on incidence greater than 80° , where the interference is constructive and the electric field is enhanced.

Figure 3.9: Schematic showing light reflection at a metal surface covered with a thin layer of polymer in PM-IRRAS for a) P polarization and b) S polarization.

Due to the absence of the electric field with S polarization at the metal surface, the S-polarized beam contains indeed only information about air and humidity. On the other hand, the P polarized beam contains information on both the gas phase and the surface. Then, detecting the reflected beam for the two polarizations (R_S and R_P) allows disentangling the spectral contributions of air and sample (Figure 3.9).

3.3.6. Reflectance and Angle Resolved Transmittance

The techniques used for the optical characterization of the DBR structures were used for both nanocomposite and crystalline systems. For all the samples, optical characterization consisting in the measurement of surface reflectance and angle resolved transmittance were performed. These analyses allow to define the optical properties of the samples and to assess their quality in terms of reflectivity and absence of light scattering phenomena.

The optical characterization of all the DBRs was performed with home-made optical setups. A y-fiber probe was used for the reflectance measurement. The reflectance probe is made by a bundle of 7 fibers, 6 connecting the light source to the sample and 1 for light collection, which connects the sample to the detector (Figure 3.10). The fiber is coupled to an AvaSpec-2048 spectrometer (200–1150 nm, resolution 1.4 nm) for UV-Vis measurement and to an Arcoptics FT-interferometer (900–2600 nm, resolution 8 cm⁻¹) for the near-infrared spectral range. The light source is a halogen-deuterium Micropak DH2000BAL. The setup allows measuring a wide spectral range (200 nm to 2600 nm) with good resolution.

Figure 3.10: Schematic of the experimental setup used for normal incidence reflectance measurements.

Angle resolved transmittance were collected for both P and S polarization with the system illustrated in Figure 3.11 and using the light source and detectors described above. Here, the light is focused on the sample using collimating

lenses. A polarizer is placed between the collimation system and the sample, which is mounted on a rotating goniometer. After the sample, the beam is collimated into a collecting fiber to the detector. For this system, considering the sample as a surface laying on the XY plane and the normal incidence as the z direction, we define P polarization when the electric field oscillates perpendicularly to the DBR plane and S polarization when the electric field is parallel to it (see Paragraph 1.3.3.1 for further details).

Figure 3.11: Optical setup used for angle resolved transmittance measurements.

3.3.7. DBR Optical Response to Vapors

The optical response of the DBRs to vapor analytes was assessed with a system similar to the one shown in Figure 3.10. In this case, the reflectance probe is substituted by an immersion probe endowed with a small open chamber containing a reflecting mirror (see photograph in Figure 3.12 a and Figure 3.12 b). The probe is connected to a halogen-deuterium Micropak DH2000BAL light source on one side, and to one of the spectrometers described above on the other side. Both the spectrometers allow to monitor the time evolution of the sample response collecting the data at set time intervals. The sample is positioned within the probe chamber with a tilting angle of $\sim 10^\circ$ to avoid collection of direct reflection from the sample surface (Figure 3.12 a and green arrow in Figure 3.12 b). The collected signal consists of the sum of the light transmitted back and forth

from the mirror through the sample (blue and red arrows in Figure 3.12). The optical response to vapor analytes is measured immersing the probe containing the sample into a sealed glass tube in room environment at 20 °C and 1 atm, where 0.5 ml of VOC liquid were previously placed to saturate the atmosphere (Figure 3.12 a).

Figure 3.12: Transflectance sensing measurement set-up a) photograph and b) schematic.

3.4. DBR Modeling

To evaluate the phenomena occurring within the DBRs during analyte intercalation, a Matlab[®] software based on the transfer matrix method was developed. To speed up the calculations, a slightly different approach than the classical one described in reference¹⁶ was used. This method considers both the electric field (E) and its derivative (F) in a structure where the refractive index suddenly change along the z direction at $z = 0$ (Figure 3.13).

Figure 3.13: Schematic of a wave propagating in a DBR along the z direction with angle of incidence θ .

In the transition between $z < 0$ and $z > 0$, the components of E and F which are tangential to the plane xy are conserved

$$E(z) = E^+ e^{ikz} + E^- e^{-ikz} \quad (3.3)$$

$$F(z) = \frac{\partial}{\partial z} E(z) = ikE^+ e^{ikz} + ikE^- e^{-ikz} \quad (3.4)$$

We can then define the fields at $z = 0$ with vectors

$$\begin{pmatrix} E(0^+) \\ F(0^+) \end{pmatrix} = \begin{pmatrix} E(0^-) \\ F(0^-) \end{pmatrix}, \quad (3.5)$$

which are not affected by the interface. Conversely, for a translation within a medium, we define

$$\gamma_S = n_1 \cos \theta_1 \quad \text{and} \quad \gamma_P = n_1 / \cos \theta_1 \quad (3.6)$$

For S and P polarization, and

$$\delta = d_1 k_{z1} = \frac{2\pi}{\lambda}. \quad (3.7)$$

Then, the translation of a distance d within the same media is given by:

$$\begin{pmatrix} E(z+d) \\ F(z+d) \end{pmatrix} = M_d \begin{pmatrix} E(z) \\ F(z) \end{pmatrix} = \begin{bmatrix} \cos \delta & \frac{i \sin \delta}{\gamma} \\ i \gamma \sin \delta & \cos \delta \end{bmatrix} \begin{pmatrix} E(z) \\ F(z) \end{pmatrix}. \quad (3.8)$$

The sample reflectance and transmittance can be computed from the global transfer matrix (M) as a product of the matrices assigned to every single layer, and using:

$$R = \left| \frac{\gamma_0 M_{11} + \gamma_0 \gamma_t M_{11} - M_{21} - \gamma_t M_{22}}{\gamma_0 M_{11} + \gamma_0 \gamma_t M_{11} + M_{21} + \gamma_t M_{22}} \right|^2 \quad (3.9)$$

$$T = \frac{n_0}{n_t} \left| \frac{2\gamma_0}{\gamma_0 M_{11} + \gamma_0 \gamma_t M_{11} + M_{21} + \gamma_t M_{22}} \right|^2 \quad (3.10)$$

3.4.1. Matlab® Code

The transfer matrix method described above was used in a Matlab® code to calculate the DBRs transmission and reflection spectra given a series of parameters. The software inputs are:

- A vector (L) containing the wavelength sampled with interval (IL).
- A vector containing the angles of incidence (T) sampled with interval (IT).
- The geometrical thickness of the substrate (d_s), low (d_l) and high (d_h) refractive media.
- Three vectors containing the complex refractive index dispersion of the two dielectric media (n_l, n_h) and of the substrate (n_s).
- The geometry of the system in terms of number of periods.

Given these inputs, the software calculates the global matrix for the given geometry and returns three matrixes with size $T \times L$, which contains the

reflectance and transmittance spectra for P and S light polarization, as well as for unpolarized light.

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Chapter 4

Nanocomposite DBR Vapor Sensors

This Chapter demonstrates highly permeable nanocomposite distributed Bragg reflector sensors made of cellulose acetate and polystyrene matrices loaded with ZnO nanoparticles. The first part focuses on the optical and mechanical properties of thin nanocomposite films. Following, the response of the sensor to toluene vapors in terms of sensitivity and reversibility is investigated. In this part, the kinetic of the process is also studied via transfer matrix method simulations. Last, the sensor selectivity to three aromatic homologues and carbon tetrachloride is discussed.

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4.1. Nanocomposite DBR Sensors

This part of the project focuses on the implementation of permeable polystyrene-ZnO nanoparticles nanocomposite in standard DBR to increase permeability to vapor analytes. To achieve this goal, flexible free-standing polymer DBRs made of cellulose acetate (CA, $n \approx 1.46$) and polystyrene (PS, $n \approx 1.57$) loaded with functionalized ZnO nanoparticles (NP, $n \approx 1.98$) were fabricated by spin-coating deposition (Figure 4.1). In this design, the filler introduces free volume in the polystyrene matrix, increasing its permeability to vapors.¹ ZnO nanoparticles were synthesized by ultrasound assisted solvothermal reaction and functionalized to be dispersed in polystyrene. The new nanocomposite was then incorporated in PS - CA DBR.

Figure 4.1: Schematic and actual photograph of a flexible DBR fabricated with cellulose acetate and polystyrene-ZnO nanoparticles nanocomposite.

4.2. ZnO-Polystyrene Optical Nanocomposite

The optical nanocomposite (NC) was prepared by dynamic spin-coating of ZnO nanoparticles dispersion in polystyrene-toluene solutions. The nanoparticles were synthesized by a solvothermal route (see Paragraph 3.2.1). Powder XRD pattern shows peaks at angles 2θ : 31.7, 34.3, 36.3, 47.5, 56.6, 62.9 and 68.1,

corresponding to Wurtzite crystallographic orientations (100), (002), (101), (102), (110), (103) and (112). The pattern indicates 13 nm crystallites as derived from Debye-Scherrer data treatment (Paragraph 3.3.1 and Figure 4.2 a). This data is confirmed by SEM analysis showing an average size of 14 nm.

Figure 4.2: a) ZnO nanoparticles powder XRD pattern and b) SEM micrograph.

To achieve good dispersion within the polystyrene matrix, the particles were grafted with a monolayer of DMMOS (see Paragraph 3.2.1). Figure 4.3 a and b compare the SEM images for thin polystyrene film loaded with 2.5% V/V_{PS} of bare and grafted nanoparticles. While several aggregates of few microns in size are visible in the film prepared with bare nanoparticles, the surface of the film with the grafted particles is smoother. Grafting allows the reduction of the aggregate number and dimension from $\sim 12000 \text{ mm}^{-2}$ with average diameter of $1.1 \text{ }\mu\text{m}$ to $\sim 2300 \text{ mm}^{-2}$ with average diameter of $0.4 \text{ }\mu\text{m}$. Negligible light scattering is thus expected from the grafted material.

Figure 4.3: SEM micrographs of nanocomposite thin films loaded with: a) bare ZnO nanoparticles and b) particles grafted with DMMOS.

The complex refractive index ($\tilde{n}=n+ik$) of the nanocomposite thin film confirms that light scattering is negligible. Indeed, the background of the absorption coefficient dispersion is zero for both the polystyrene and the nanocomposite thin films. The nanocomposite refractive index ($n=1.587$ at 800 nm) is only $\sim 0.5\%$ higher than the one of polystyrene ($n=1.581$ at 800 nm), in agreement with the effective medium theory.² The actual dispersion of the ZnO nanoparticle refractive index near the excitonic peak is embedded in the overall effective medium response due to the relatively low nanoparticles load. ($2.5\% V/V_{PS}$).

Figure 4.4: Refractive index (dash line) and extinction coefficient (full line) dispersions for bare polystyrene (green) and nanocomposite (red) thin films.

The increase of permeability induced by the load was evaluated by permeation of helium on free-standing nanocomposite and bare polystyrene thin films. Figure

4.5 shows that the permeability of polystyrene is very low, and does not depend on the applied pressure. This behavior is due to the non-porous nature of the polystyrene film, and is typical of amorphous polymers.^{3, 4} Remarkably, the nanocomposite is 3.5 times more permeable and shows strong dependence on applied pressure. Such permeability increase is attributed to free-volume at the nanoparticles-polystyrene interface, which facilitates gas permeation.

Figure 4.5: Permeability to Helium of polystyrene (green dots) and nanocomposite (red squares) films as a function of applied pressure.

4.3. Optical Characterization

DBRs were fabricated by alternated spin-coating deposition of cellulose acetate and nanocomposite with ZnO nanoparticles concentration of 2.5% V/V_{PS} . Figure 4.7 shows the experimental and calculated spectra for a DBR made by 15 periods. The spectrum was modelled as described in Paragraph 3.4. The layer thicknesses were measured by interferometric microscopy on single and double polymer layers spun-cast on glass substrates under the same DBR condition (see Paragraph 3.3.3). The outcome of the measurement is 378 nm for the nanocomposite and of 92 nm for cellulose acetate (Figure 4.6).

Figure 4.6: a) Cellulose acetate and b) nanocomposite monolayer and bilayer thicknesses determined by interferometric microscopy.

Figure 4.7 (red line) shows the spectrum of a 15+1 periods DBR with maximum reflectance peaks at 1505 nm, 758 nm, 506 nm, 386 nm, and 317 nm, corresponding to the stop-band and its higher order replicas. For the sensing measurement Analysis of the optical response first order stop-band was used for sensing of vapor analytes. The baseline of the spectrum shows a Fabry-Pèrot interference pattern, which arises from the interference among beams partially reflected from the top and bottom DBR surfaces, and indicates that the system show negligible light scattering and high optical quality structures. The good agreement between experimental and simulated spectra in Figure 4.7 confirms the excellent optical quality of the multilayer. Minor discrepancies appear in the UV spectral range, where thickness variations, refractive index precision, and spectrometer sensitivity become critical.

Figure 4.7: Comparison between experimental (black) and calculated (red) reflectance spectra of a 15 periods nanocomposite – cellulose acetate DBR.

Figure 4.8 a shows the nanocomposite DBR transmittance spectra recorded as a function of incidence angle for P and S light polarizations. For both polarizations, the peaks blue shift increasing the angle of incidence. While in S polarization the peak width is nearly independent of the angle, in P polarization both width and intensity of the peaks decrease toward the Brewster angle. This is consistent with the assignment of stop-bands and fully agrees with the calculated data of Figure 4.8 b and theoretical predictions reported in Paragraph 1.3.3.

Figure 4.8: a) Experimental and b) calculated transmittance spectra contour plot as a function of light incidence angle for light polarization P (top panel) and S (bottom panel).

4.4. Sensor Response

To evaluate the sensing performance of the DBR, the sample was exposed to toluene vapor as described in Paragraph 3.3.7, and its optical response was compared to that of a reference sample fabricated using bare polystyrene using the same conditions (Figure 4.9). In the case of the nanocomposite (Figure 4.9 a), the transmittance spectra show a remarkable shift of the stop-band of ~50 nm after 15 minutes of exposure (Figure 4.9 b), and a ~20% reduction of stop-band intensity in differential transmittance (Figure 4.9 c). Conversely, no significant changes are observed in either transmittance or differential transmittance spectra of the standard PS-CA DBR over time (Figure 4.9 b' and c').

Figure 4.9: Optical response to toluene vapor of DBR sensors. Nanocomposite DBR on the left and control DBR on the right. a), a') Contour plots of the transmittance spectra collected every 5 minutes; b), b') Corresponding transmittance spectra; c), c') Time dependent differential transmittance at the initial stop-band wavelength.

The optical response of the DBR at longer exposure times is even richer. After the first 15 minutes, the transmittance peaks undergo non-monotonic spectral and intensity changes (Figure 4.10 a). The contour plot in Figure 4.10 a clearly shows

transmittance peaks assigned to the stop-band (marked by the * symbol) red shifting for the first 15 minutes (compare to Figure 4.9 a), disappearing thereafter, and reappearing after ~80 minutes at about 1850 nm (marked by the *' symbol).

Figure 4.10: a) Experimental and b) calculated contour plots of the transmittance spectra collected during the exposure.

The spectral shift of the stop-band and its intensity modulation are due to the swelling of the permeable nanocomposite layers induced by toluene molecules that penetrate in the DBR. Indeed, the optical response can be reproduced by a phenomenological model accounting for the increase of thickness of the nanocomposite layers (D_{NC}) upon permeation of vapors from the surface in contact with the toluene rich environment. Let us consider a progressive swelling of the nanocomposite layers over the time (t), while the cellulose acetate layer thicknesses (D_{CA}) remain constant:

$$D_{I,CA}(t) = D_{j,CA}(0) \quad (4.1)$$

$$D_{j,NC}(t) = D_{j,NC}(0) + \int_{t_0}^t \frac{\partial D_{j,NC}(t)}{\partial t} dt \quad (4.2)$$

Under these assumptions, the thickness of each nanocomposite layer j increases over time according to its swelling velocity ($v_j = \partial D_{j,NC}(t)/\partial t$).

The system of equation 4.1 and 4.2 was solved numerically for discrete time intervals, using the initial layer thicknesses measured by interference microscopy (Figure 4.6) as boundary conditions and arbitrarily setting time scale to fit the experimental data.

Note that this model makes two assumptions: i. The thickness of cellulose acetate layers does not vary with time, and permeation across these layers occurs instantaneously (introducing a time delay due to permeation across cellulose acetate layers would not affect the swelling velocities v_j and their physical meaning). ii. The variation of both cellulose acetate and nanocomposite refractive index upon permeation of solvent vapors is accounted by the variation of the effective optical thickness ($\partial D_{j,NC}(t)/\partial t$), which is defined as the product $D_j n_j$.

The time evolution of the thickness of each nanocomposite layer and swelling velocities derived from the model are reported in Figure 4.11. The thickness of the first layer increases quickly upon toluene exposure; its swelling velocity is very fast initially due to permeation of toluene, and then decreases (Figure 4.11 b) until the thickness becomes ~25% larger than the original value (Figure 4.11 a). Toluene penetrates progressively into the inner layers of the structures, which then undergo similar process. After about one hour, the outermost half of the DBR is fully swollen while the innermost half is still swelling. Steady-state is reached only after several hours of exposure.

The calculated layer thicknesses were used to model the time evolution of the spectral response of the DBR. The good agreement between experimental (Figure 4.10 a) and calculated (Figure 4.10 b) spectra indicates that the model can capture the macroscopic physical changes of the sample, and that progressive swelling of the DBR layers is indeed responsible for the spectral shift of the stop-band. Permeation of toluene vapors across the DBR layers modifies their optical thickness, resulting in a rather complicated but predictable evolution of the

transmittance spectra. Within the first 15 minutes of exposure, the stop-band peak red shifts due to the thickness increase of the top DBR layer (Figure 4.9 a and marked by the symbol * in Figure 4.10 a and b). Upon analyte penetration in the underlying layers, the diffraction patterns of differently swollen films interfere destructively, and the intensity of the stop-band is progressively reduced until it cancels after ~20 minutes of exposure (Figure 4.10 a and b between the symbols * and *'). Only after ~80 minutes of vapor exposure, when a significant part of layers reaches a stationary swollen condition, the restored optical periodicity results in a new, clearly defined stop-band (Figure 4.10 a and b marked by the *' symbol). Free volume at the ZnO-polystyrene interface behaves as solvent condensation point, initiating the swelling process, which then propagates to the whole nanocomposite layer.

Figure 4.11: Evolution of the modelling parameters of each nanocomposite layer in the DBR over exposure time: a) layer thickness and b) swelling velocity.

4.5. Sensitivity

To assess the DBR sensitivity, sensor response time was related to the analyte

concentration. The method used to evaluate the response time is illustrated in Figure 4.12 and considers the time intercurring between the first and second intensity oscillation (t_1 and t_2 in Figure 4.13) at the stop-band initial wavelength (596 nm), (black line in the bottom panel of Figure 4.12). The two relative minimums were evaluated from the differential intensity calculated as $\Delta R/\Delta t$ (red line in the bottom panel of Figure 4.12).

Figure 4.12: Evaluation of DBR response time to toluene concentration. Top panel: reflectance spectra contour plot over the time for a DBR during exposure to 68 ppm of toluene. Bottom panel: reflectance intensity (black line) and differential reflectance intensity (red line) over the exposure time at 596 nm.

Figure 4.13 shows the response time to toluene concentrations ranging from 20 ppm to 120 ppm in air for DBR sensors with stop-band positioned at 590 nm. The device is sensitive in the entire concentration range, with maximum value of 8 ppm at the higher concentrations. Note that the response time decays exponentially upon increases of vapor concentration, thus confirming this sensitivity in the entire concentration range and allowing to estimate sensitivity below 0.5 ppm for concentrations lower than 70 ppm.

Figure 4.13: Response time of the nanocomposite sensor to different concentration of toluene vapor.

The time necessary for the measurement varies from 30 s (response time 13 s) for the higher vapor concentration to 60 min (response time ~33 min) for the lower concentration. The prediction and data show that the response time only depends on environmental analyte concentration and DBR layer thickness (i.e. stop-band spectral position). Indeed, response time and sensitivity can be easily modulated tuning the stop-band; devices with stop-band in the near infrared range (thicker nanocomposite layers) will possess higher sensitivity but slower response than sensors with stop-band in the visible range. On the other hand, while near infrared devices necessitate of detection system, colored DBR can be used for the qualitative assessment of vapor leakages without any equipment.

Notice that the intensity oscillations at longer time (t_3-t_2 and t_4-t_3 in Figure 4.12) occurs within shorter intervals than the oscillation used to define the sensor response (t_2-t_1 in Figure 4.12). As explained in Paragraph 5.5, every oscillation corresponds to the increase of optical thickness of a subsequent high refractive index layer, starting from the one closer to the environment. Figure 4.11 shows that together with the swelling of the top nanocomposite layer, the analyte penetrates in the second layer. On the other hand, the overall optical response cannot discriminate the swelling of the single layers, and the oscillations at longer time occurs at shorter intervals. Figure 4.14 shows the time intervals retrieved

from three subsequent intensity oscillations for a sensor with stop-band at ~ 500 nm. The response time retrieved for the first (t_2-t_1 , black), second (t_3-t_2 , red) and third (t_4-t_3 , green) oscillations can be well fitted with a first order exponential decay (continuous lines in Figure 4.14), indicating that the long-term response is predictable. This analysis can therefore provide additional parameters to enhance sensitivity and accuracy at the expenses of response time.

Figure 4.14: Response time of nanocomposite sensors retrieved from three subsequent stop-band intensity oscillations.

4.6. Reversibility

Concerning reversibility, the device optical response is easily restored with less than 2% error after several cycles of exposure and regeneration by thermal treatment at 50°C for 45 s (Figure 4.15 a and b) or by few minutes in room condition. However, the response time decreases linearly with the number of cycles performed (Figure 4.15 c).

The high reproducibility of the optical response indicates full toluene desorption and restoration of the initial layer thicknesses, while the shorter response time can be attributed to a different composite morphology which is likely to be affected from preferential paths caused by the toluene molecules. Indeed, the sensing process is somehow reversible but severe thermal treatments are required for a full recovery.

Figure 4.15: Reflectance spectra of a nanocomposite sensor a) before exposure and b) after one, two, three, four and five cycles of swelling and regeneration. c) Response time, i.e. elapsed time for the sensor optical response to evolve from situation a) to b).

4.7. Selectivity

The nanocomposite sensor selectivity to VOC was investigated by exposing the DBR to vapors of four different analytes. Four portions of the same DBR were then exposed to vapors of benzene, toluene, ortho dichlorobenzene, and carbon

tetrachloride Figure 4.16 a - d show the spectra collected during the exposure at selected time intervals, while Figure 4.16 a' - d' reports the spectra dynamics as contour-plots.

The top panel of Figure 4.16 reports the data for the sensor exposed to benzene vapors. The optical behavior of the sensor fully resembles the one already described for toluene. Indeed, the stop-band first red shifts from 450 nm to 520 nm and splits into two structures peaked at 410 nm and 480 nm (~ 2 min, marked with # in Figure 4.16 a'). This behavior corresponds to the swelling of the top DBR layer. At the same time, the vapor penetrates deeper in the structure and generates a second stop-band positioned at longer wavelength (marked with * in Figure 4.16 a'). In this case, the simultaneous presence of swollen and unaffected layers in the DBR allows to detect two stop-bands: the first is assigned to the unswollen structure at ~450 nm and the second, positioned at 530 nm, is assigned to the swollen DBR at the top. At longer exposure time, due to the further intake of benzene, the intensity of the short wavelength peak decreases (continuous arrow in Figure 4.16 a), while the intensity of the long wavelength peak increases (dashed arrow of Figure 4.16 a). Meanwhile, the spectral position of the new stop-band shifts toward the red from 530 nm to 590 nm in 8 minutes. At this time, reflectivity remains steady.

For comparison, the same Figure reports the response of the DBR to toluene, which shows nearly identical behavior. Here the stop-band red shift and split into two structure due to the swelling of the first layer (marked with # in Figure 4.16 b'). At the same time the intensity of this stop-band fades (continuous line of Figure 4.16 b) and a second stop-band, due to the swollen structure, emerges at ~510 nm (marked with * in Figure 4.13 b'). This band finally red shifts until 580 nm within 30 minutes (dashed arrow in Figure 4.13 b).

Comparing the to the two aromatic compounds, benzene induces a ~4-fold faster response and a slightly smaller red shift than toluene. The faster response is likely due to both, the higher benzene concentration in the environment and its smaller size, which would favor faster molecule intercalation within the DBR.

When the sensor is exposed to o-dichlorobenzene, the swelling of the first DBR layer can be evinced from the red shift and splitting of the band positioned at 450 nm, which occurs within the first minute of exposure (marked with # in Figure 4.16 c'). On the other hand, the intercalation of this molecule does not allow the formation a swollen DBR lattice. Indeed, after the swelling of the first layer, the stop-band intensity fades, while no other peaks are generated. Due to the large molecular size, one could expect a new stop-band strongly shifted to the red part of the spectrum. For this reason, the near infrared region (700 nm to 2600 nm) was also analyzed, but no spectral features were observed. Therefore, the intercalation of the bulky molecule seems to fully breaks the DBR periodicity, destroying the structure.

The response to carbon tetrachloride is reported in Figure 4.16 d and d'. This molecule causes similar behavior than benzene and toluene, with two major differences. First, the response is ~30 time slower than in the previous cases. Indeed, the swelling of the first layer is still visible from the red shift and splitting of the stop band (marked with # in Figure 4.16 d') within 1 h of exposure, before steady state is reached in 15 h. The second difference is in the spectral position of the swollen DBR stop-band, which appears at 530 nm (marked with * in Figure 4.16 d') and shifts up to 630 nm in 15 h.

Comparing the responses to the four VOC, one can notice that selectivity to molecules with very dissimilar structures has been achieved, however only minor differences are evinced between the response to toluene and benzene. One way to recover selectivity to specific analytes is by chemiometric analyses.⁵ However this approach requires long time and complicated data processing, which go beyond the purpose of developing a selective colorimetric sensor based on naked eye detection. The limited selectivity of the nanocomposite DBR were overcome employing poly(p-phenylene oxide) as active sensing medium in the DBR as exposed in the next Chapter.

Figure 4.16: Evolution of the nanocomposite sensor transmittance spectra acquired during exposure to vapor of a) benzene, b) toluene, c) o-dichlorobenzene and d) carbon tetrachloride.

4.8. Outcomes

This Chapter demonstrated new polymer DBR sensors with high optical responsivity to benzene, toluene, ortho dichlorobenzene and carbon tetrachloride vapor exposure. Vapor sensitivity was enhanced by increasing the overall DBR permeability with a new polystyrene-ZnO nanocomposite, attaining permeability 3.5 time higher than bare polystyrene. DBRs displaying up to the fifth diffraction order were fabricated by simple spin-coating of alternated layers of cellulose acetate and the nanocomposite material, which have slightly higher refractive index than bare polystyrene. The comparison between nanocomposite and bare DBR sensing performance shows that the filler induces a ~10 time faster optical response to toluene vapor exposure, leading to fast detection of toluene vapor concentration ranging between 20 to 120 ppm in air with sensitivity below 10 ppm. The improvement in optical response is due to presence of free-volume induced by the loaded nanoparticles, which allows faster swelling of the nanocomposite thin films. The complex dynamics of vapor permeation and swelling of each DBR layer is fully understood in terms of a simple analytical model, which allows predicting the overall DBR optical response up to very long time of exposure to the target vapor. Label-free selectivity to vapors of VOC with dissimilar molecular structure was also demonstrated.

4.9. References

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Chapter 5

Clathrate DBR Vapor Sensors

This Chapter focuses on the use of amorphous poly(p-phenylene oxide) as a permeable medium in all-polymer distributed Bragg reflector sensors. The first Paragraph describes the preparation of amorphous thin films with good optical quality and suitable for the fabrication of Bragg stack sensors. Such sensors are then demonstrated possessing high vapor permeability, and selective optical response to benzene, toluene, o-dichlorobenzene and carbon tetrachloride vapors.

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5.1. Clathrate DBR Vapor Sensors

This Chapter reports an alternative approach to overcome the low permeability typical of amorphous polymers while allowing label-free selectivity to vapors of VOC with very similar molecular structures. As explained in Chapter 1, the selectivity is achieved exploiting the ability of amorphous poly(p-phenylene oxide) (PPO) to uptake large amount of guest molecules and to form co-crystalline phases with distinct optical properties. The penetration of certain molecules within amorphous PPO induces the formation of co-crystalline phases where guest molecules are included within the polymer lattice. Guest desorption results in the formation of a typical nanoporous crystalline phase.¹⁻⁴ The different optical properties of co-crystalline and nanoporous crystalline phases deeply modify the DBRs reflectance spectrum throughout the visible spectral range, inducing chromatic changes that can be detected by the naked eye. As a proof of principle, the characteristic optical response of a PPO-CA DBR to vapors of carbon tetrachloride, benzene, toluene, and o-dichlorobenzene is reported.

5.2. Fabrication of Amorphous and Crystalline PPO Thin Films

Polymer DBRs require as building block thin films with good optical quality that induce limited light scattering. In principle, the spin coating deposition of PPO solutions can induce the formation of a semi-crystalline phase containing grain boundaries that scatter light, because most of the solvents suitable for the PPO deposition allow its crystallization.¹⁻⁴ This Paragraph describes the spin-coating conditions that allow formation of suitable amorphous PPO films by analyzing the infrared spectrum and the optical constants of samples spun-cast from toluene and carbon tetrachloride solutions.

Figure 5.1 shows the ATR spectra of PPO films spun-cast from the two solvents in the region between 800 cm^{-1} and 900 cm^{-1} , where the shift toward lower energy, and sharpening of the peaks assigned to the in-phase (860 cm^{-1}) and the

out-of-phase (831 cm^{-1}) out-of-plane -CH wagging are known fingerprints of amorphous and crystalline PPO in bulk samples.⁵⁻⁷ The ATR spectra show the out-of-phase -CH wagging signal centered at 831 cm^{-1} for the sample prepared from toluene solution, and at 826 cm^{-1} for the one spun-cast from carbon tetrachloride. The in-phase wagging mode is positioned at 855 cm^{-1} for toluene and 853 cm^{-1} for carbon tetrachloride. For carbon tetrachloride, the two bands are sharper. The data, in agreement with literature,^{3,6} indicate that the spin-coating from carbon tetrachloride yields crystalline PPO, while thin-films fabricated from toluene solution include the amorphous phase.

Figure 5.1: ATR spectra of PPO thin films spun-cast from toluene (green) and carbon tetrachloride (black) solutions.

The thin film refractive indexes retrieved from ellipsometry provide additional information about the PPO phases. Figure 5.2 shows that the refractive index of a PPO film cast from toluene ranges from 1.84 at 250 nm to 1.56 at 2000 nm. When PPO is deposited using carbon tetrachloride, its refractive index is lower and ranges from 1.84 at 250 nm to 1.54 at 2000 nm. This reduction is related to the lower density of the nanoporous crystalline phase ($\sim 1.009\text{ g/cm}^3$) compared to the amorphous phase ($\sim 1.016\text{ g/cm}^3$).⁵ The same Figure reports also the dispersion of the optical function determined for cellulose acetate thin films, which agrees well with previous reports.⁷

Figure 5.2: Refractive index dispersion of cellulose acetate (cyan), and PPO thin films spun cast from toluene (green) and carbon tetrachloride (black).

Figure 5.3 compares the transmittance spectra of two DBRs made by 10+1 periods of cellulose acetate and PPO cast from the two solutions under the same conditions. The DBR spun-cast from toluene shows a minimum of transmittance of ~50% at 640 nm and a strong interference pattern demonstrating its good optical quality (green line). When carbon tetrachloride is used, the first order stop-band is red shifted to 1070 nm and its intensity is ~65%. The sample also shows higher order stop-band replicas positioned at $\lambda_B/2=520$ nm and $\lambda_B/3=380$ nm and an interference pattern characterized by low intensity and periodicity. The broad and relatively weak stop-band of this sample is caused by the presence of the crystalline phase. The shift toward longer wavelength caused by carbon tetrachloride suggests that the resulting film thickness is larger than with the aromatic solvent. This effect is attributed to the low boiling point of carbon tetrachloride ($T_{b-TOL}=111^\circ\text{C}$ $T_{b-CTC}=77^\circ\text{C}$), which allows faster solvent evaporation during spin-coating and substantial withholding of the polymer on the surface of the sample.

Figure 5.3: Transmittance spectra of CA-PPO DBR fabricated with toluene (green) and carbon tetrachloride (black) PPO solution using the same preparation conditions.

These data clearly show that amorphous PPO film can be obtained by spin coating from toluene solution. Moreover, DBRs containing a crystalline phase overcoming the light scattering phenomena associated to grain boundaries that usually hinder the formation of the diffraction pattern were also obtained.

5.3. Vapor Induced Phase Transition in Amorphous PPO Thin Films

Before embedding PPO into DBR sensors, crystallization of the thin film in the presence of VOC vapors was assessed. Figure 5.4 reports the IRRAS spectra of the polymer films before (black line) and after crystallization by exposure to VOC vapors for 30 minutes at room temperature. Figure 5.4 shows that vapors induce the crystallization of all the samples. The out-of-phase wagging mode assigned to amorphous phase at 831 cm^{-1} shifts to 828 cm^{-1} for films exposed to carbon tetrachloride (magenta), and to 826 cm^{-1} for films exposed to the aromatic compounds (red for benzene, green for toluene and blue for *o*-dichlorobenzene). In the new structure, this characteristic peak broadens, indicating the coexistence of an amorphous and a crystalline phase in the PPO thin films.^{8 8} The in-phase wagging mode moves from 860 cm^{-1} to 858 cm^{-1} ; it becomes sharper upon vapor exposure, indicating the occurrence of crystallization.

Figure 5.4: IRRAS spectra of PPO thin films before (black line) and after crystallization induced by: carbon tetrachloride (magenta), benzene (red), toluene (green) and *o*-dichlorobenzene (blue).

5.4. PPO-CA Distributed Bragg Reflectors

Phase-changing amorphous PPO films were then used as the active sensing region of all-polymer DBRs. Figure 5.5 a shows the architecture of the DBR grown by spin-coating deposition of 21 alternated thin films of PPO and cellulose acetate. Figure 5.5 b shows the photograph of a 30 mm diameter sample with vivid green color generated by the DBR stop-band. The stop-band is in turn detectable in the spectra of Figure 5.5 c as an intense peak of reflectance centered in the green region of the visible spectrum ($\lambda \sim 560$ nm). The nearly perfect superposition of the spectra collected over different spots on the sample surface (see inset of Figure 5.5 c) proves the large homogeneity of the DBR. Furthermore, the background of all the spectra shows a Fabry-Pèrot interference pattern that further reveals the excellent optical quality of the structures.

Figure 5.5: a) Schematic, b) photograph and c) reflectance spectra collected at six different locations of the sample for a CA–PPO DBR.

Figure 5.6 shows the DBR angle resolved transmittance spectra for S and P light polarizations (see Paragraph 3.3.6). Increasing the angle of incidence, the stop-band, blue shifts for both light polarizations. For S polarization, its intensity increases, while for P polarization, it decreases toward the Brewster angle, in agreement with the theoretical prediction reported in Paragraph 1.3.3.

Figure 5.6: Contour-plots of CA-PPO DBR angle resolved transmittance spectra for S (left panel) and P (right panel) light polarizations.

5.5. DBR Response to Toluene Vapors

The responsivity of the DBRs to vapor was tested by monitoring the evolution of its transfectance spectrum during exposure to toluene. Figure 5.7 a reports the spectra collected every 3 min during exposure, while Figure 5.7 b shows the full spectrum evolution as a contour plot. The DBR stop band is initially positioned at 560 nm and splits into two structures with minimum of intensity at 542 nm and 599 nm within the first few minutes of exposure (dashed black in Figure 5.7 a).

Figure 5.7: Optical response of CA-PPO DBR to toluene. a) Transflectance spectra collected every 3 minutes. b) Contour plots of the transfectance spectra dynamics. c) Photograph of the sample before (top) and after (bottom) exposure.

This behavior has been previously discussed for the nanocomposite sensors in Chapter 4, and takes place when the analyte penetrates within the first PPO layer causing it to swell, or modifies its refractive index. In this case, the swollen PPO capping layer film does not meet the DBR periodicity conditions and does not contribute to the stop-band. Effectively, it is as if this layer would be physically removed from the DBR structure. Consequently, the stop-band shape is similar to the one of a DBR with the cellulose acetate top layer (Figure 5.8).

Figure 5.8: Reflectance spectra of a PPO-CA DBR with different number of layers. a) Spectra of the DBR with PPO top layer. b) Spectra of the DBR with CA top layer.

At longer exposure time, the stop-band monotonically red shifts until 738 nm within 1 h, when the steady-state equilibrium condition is reached. During this time, its intensity slightly decreases in the time interval between 4 and 14 min (marked with + in Figure 5.7 b). Figure 5.7 c also shows a photograph of the DBR

surface before (top panel) and after (bottom panel) the exposure. Here the color change is easily detectable as a shift from green to red.

5.6. Label-Free Selectivity to VOC Vapors

The DBRs capability to selectively detect VOC was assessed by exposing four portions of a sample to saturated environments of carbon tetrachloride, benzene, toluene and *o*-dichlorobenzene vapors. The evolution of the transfectance DBR spectrum was monitored over time during guest absorption (see Paragraph 3.3.7). Figure 5.9 a - d show the evolution of the spectra at selected exposure times. Figure 5.9 a' - d' and a'' - d'' show the spectral contour-plots for selected spectral ranges and time domains: the stop-band (with lower transfectance value) is visible in red color tones, while the background (with higher transfectance value) is in blue tones.

Figure 5.9 shows that vapor exposure induces a red shift of the DBR stop-band with diverse magnitude and kinetic for the four VOC. In the case of benzene, the exposure induces the progressive swelling of PPO layers. The spectral response globally consists of the red shift of the stop-band $\Delta\lambda_{\text{BEN}} = 189 \text{ nm}$, which occurs within 1h of exposure. The spectral evolution is also characterized by the destruction and reconstitution of the DBR periodicity. In details, the stop-band red shifts by $\sim 20 \text{ nm}$ during the first 15 s of exposure (marked by * in Figure 5.9 a'), and then splits into two structures peaked at 535 and 570 nm (continuous arrow in Figure 5.9 a and # Figure 5.9 a') after $\sim 50 \text{ s}$ of exposure. As mentioned above, this behavior takes place when the analyte penetrates within the first PPO layer. At longer exposure time, the vapor penetrates more deeply into the DBR inducing the swelling of the layers immediately below the top one, while the bottom structure (close to the glass substrate) remains unaffected. The first stop-band is visible at $\sim 560 \text{ nm}$ (un-swollen bottom structure) and the second at $\sim 710 \text{ nm}$ (swollen top DBR), marked with + and +' in Figure 5.9 a''. Before reaching

the stationary condition, the top layers have different thickness. Consequently, the stop-band positioned at longer wavelength is spectrally broad. With further benzene uptake, the intensity and symmetry of this peak keep increasing. Meanwhile, the benzene molecules diffuse to the bottom DBR layers and the intensity of the stop-band positioned at shorter wavelength starts fading. Indeed, after ~12 minutes of exposure only the long-wavelength peak is visible (dashed arrow in Figure 5.9 a and a''). At longer times, the DBR keeps absorbing benzene until all the layers are fully swollen and the new stop-band further red shifts by additional 30 nm. This behavior was also observed for the progressive swelling of nanocomposite DBRs and reported in Chapter 4.¹³

As discussed in the previous Paragraph, the optical response of the DBR to toluene is simpler and is characterized by the presence of a single stop-band monotonically moving to the red part of the visible spectrum. Here the stop-band, initially centered at 560 nm, undergoes a sudden red shift to 600 nm at ~8 s of exposure (marked with * in Figure 5.9 b') and then slowly shifts monotonically until ~740 nm ($\Delta\lambda_{\text{TOL}} = 191$ nm) in about 1 h (sashed arrow in Figure 5.9 a and a''). In the case of *o*-dichlorobenzene, the spectral response has the same discontinuous behavior observed for benzene, but the stationary condition is reached within 2 h of exposure showing that the kinetics is much slower, while the stop-band red shift is larger than in the previous case $\Delta\lambda_{\text{DCB}} = 257$ nm. Even in this case, the swelling of the capping layer can be observed as a stop-band red shift (* mark in Figure 5.9 b') and splitting (# mark in Figure 5.9 b') occurring after ~5 minutes of exposure. At longer exposure time, the vapor penetrating the structure progressively destroys the DBR, thus reducing the intensity of its stop-band within 25 minutes (marked with + in Figure 5.9 b''). At longer time, the periodicity condition is restored and a broad structure, assigned to the swollen layers, arises at about 820 nm (+' mark in Figure 5.9 b''). The further penetration of *o*-dichlorobenzene, shifts the stop-band of other 100 nm within 120 min of exposure (dashed arrow in Figure 5.9 b and b''). The large red shift of the stop-band is attributed to the higher molecular hindrance of *o*-dichlorobenzene, which

is likely to prompt a large swelling of the DBR layers. Such strong thickness variation also decreases the interfacial tension between PPO and cellulose acetate layers, inducing the inhomogeneous broadening of the stop-band.

When the sensor is exposed to carbon tetrachloride, the equilibrium condition occurs on a much longer time scale than for the three aromatic homologues. The swelling of the PPO capping layer occurs within the first minute of exposure (* and # marks in Figure 5.9 c' highlight the stop-band red shift and splitting). At the same time, a broad second structure is generated at ~ 750 nm (+ mark in Figure 5.9 c''). After that, the system keeps evolving slowly. After 22 h in the carbon tetrachloride environment, the intensity of the stop-band assigned to the un-swollen DBR fades, while the stop-band arising from the top swollen layers increases in intensity and symmetry (dashed arrow in Figure 5.9 c and c''). Globally the stop-band shows a shift of $\Delta\lambda_{\text{CTC}} = 235$ nm.

The selective optical response of the sensor is clearly represented by the circular insets of Figure 5.9 showing the actual photographs of four samples before and after ~ 40 min of exposure. The sensor exposed to benzene appears initially green while, after the exposure, the color changes to a vivid and bright red due to the stop-band now positioned in the red region. Differently, Figure 5.9 b shows that, when exposed to *o*-dichlorobenzene, the sensor appears reddish with a much darker tone compared to the previous case. This difference is attributed to the formation of a swollen structure with a spectrally broad stop-band positioned in the near infrared part of the spectrum. Figure 5.9 c shows that the color of the sample exposed to carbon tetrachloride changes slightly. The sample surface appears green with some reddish shadow. At 40 min of exposure, the slow response of the sensor to carbon tetrachloride vapors allows the coexistence of two stop-bands: the one related to the unswollen top layers in the green region and a broader one centered in the near infrared region. These differences are also highlighted in Figure 5.10, which reports the evolution of the spectrum of all samples within the same spectral and time domains.

BENZENE **TOLUENE** **ORTHO DICHLOROBENZENE** **CARBON TETRACHLORIDE**

Figure 5.9: Time resolved optical response of PPO- CA DBR to a) benzene, b) toluene, c) o-dichlorobenzene and d) carbon tetrachloride. a' - d') Contour plots of the transflectance spectra initial dynamics. a'' - d'') Long-term dynamics.

Figure 5.10: Contour plots of the DBR transfectance during 25 minutes of exposure for a) benzene, b) toluene, c) o-dichlorobenzene, and d) carbon tetrachloride.

Comparing the response of the nanocomposite DBR reported in Chapter 4, and PPO DBR the four VOC vapors, three major differences in their optical response can be evinced:

- At saturation, the stop-band of PPO sensor undergoes a red shift ($\Delta\lambda$) of $\Delta\lambda_{PPO\ BEN} = 189$ nm, $\Delta\lambda_{PPO\ TOL} = 191$ nm, $\Delta\lambda_{PPO\ ODB} = 257$ nm and $\Delta\lambda_{PPO\ CTC} = 235$ nm. For nanocomposite sensors, the observed shift is $\Delta\lambda_{NC\ BEN} = 138$ nm, $\Delta\lambda_{NC\ TOL} = 136$ nm, $\Delta\lambda_{NC\ CTC} = 167$ nm, while o-dichlorobenzene penetration destroys the lattice. In both sensors, benzene and toluene induce comparable shifts, while the other molecules induce a stronger and different variation.
- Despite the stop-band of the DBR exposed to benzene and toluene undergo a similar shift in both nanocomposite and PPO sensors, in the case of PPO the spectral response to the two vapors is very different. Indeed, while benzene

vapors break the lattice periodicity (marked with + and +’ in Figure 5.9 a’), toluene causes a monotone red shift of the stop-band (Figure 5.9 b’). This allows recognizing the two analytes.

- In PPO sensors, benzene, toluene and carbon tetrachloride induce swollen photonic structure with symmetric stop-bands and well-defined interference patterns (Figure 5.10 a, b and d). Conversely, *o*-dichlorobenzene causes inhomogeneous broadening and Fabry-Pèrot fringes are absent (Figure 5.10 c). This behavior is attributed to the hindrance of *o*-dichlorobenzene, which similarly disrupted the photonic structure of nanocomposite sensors (Figure 4.16).

5.7. Long-Term Response

All spectral variations observed in Figure 5.9 are due to the formation of different PPO co-crystalline phases with the different guests.^{5,6} This is reflected by the sensor response at long time (i.e. 24 h after the initial exposure). The black line in Figure 5.11 is the initial reflectance spectrum of the DBR. As mentioned above, it shows a stop-band at $\lambda=556$ nm with reflectance intensity $R=55\%$ and typical interference pattern.

Independently of the VOC guests, the stop-band does not return to the initial condition after exposure and desorption of the guest. When benzene is desorbed, its intensity is indeed reduced to 36% while its spectral position remains red shifted to 584 nm ($\Delta\lambda=28$ nm, red line in Figure 5.11). The interference pattern in the spectrum is well defined, indicating that the initial optical quality of the system is unchanged. Conversely toluene desorption allows a much smaller shift of the stop-band ($\Delta\lambda \cong 9$ nm) and slightly lower intensity (33%). After *o*-dichlorobenzene desorption, the interference pattern is irregular and has low intensity. The stop-band is strongly shifted to 639 nm ($\Delta\lambda \cong 83$ nm), and its intensity approaches 22%. Moreover, the peak is characterized by the inhomogeneous spectral broadening induced by the strong swelling of the PPO

layers detected during the exposure (Figure 5.11). These features indicate that the bulky molecule strongly affects the photonic structure even at long-time scales. In comparison, desorption of carbon tetrachloride induces a stop-band with intensity of 33% positioned at 577 nm ($\Delta\lambda = 11$ nm).

Comparing the data collected after VOC desorption with the IRRAS spectra of Figure 5.4, one can reasonably conclude that, on the long-term, the PPO layers retain a nanoporous crystalline phase with lower density and thus lower refractive index than the pristine amorphous films. The lower refractive index is indeed responsible for the decrease in intensity of the DBR stop-band after guest desorption (see Paragraph 1.3.3.2). Red-shift of the stop-band also confirms the presence of nanoporosity typical of the crystalline structure. The low density phase has indeed higher volume and thickness than the initial amorphous layers.⁸ The strong red shifts observed in Figure 5.9 for all the VOC guests can then be attributed to two phenomena: the formation of co-crystalline phases including guest molecules and the swelling of the amorphous phase already observed for the nanocomposite systems.

Figure 5.11: Reflectance spectra of PPO-CA sensors before exposure (black) and after exposure and desorption for 24 h of benzene (red), toluene (blue), o-dichlorobenzene (blue) and carbon tetrachloride (magenta) vapors.

Overall, despite the lack of reversibility, the low material and fabrication costs, together with the small substrate size necessary for sensing (down to 2-3 mm²) and the fast and high throughput fabrication processes available,⁹ make the use of disposable polymer DBR sensors viable from both economically and operative points of view. Moreover, the irreversible nature of the PPO phase transition allows label-free selectivity even to vapor of molecules with very similar structure. Such selectivity has never been achieved without appropriate chemical functionalization of the photonic crystal. Polymeric DBRs based on phase-change active layers, such as those demonstrated in this work, pave the way for new generation colorimetric sensors with broad selectivity and that do not require any instrumentation other than the naked eyes for detection. Such sensors would enable extensive and constant monitoring of VOC pollution in offices and households directly by the end users.

Notwithstanding reversibility is usually advantageous for a sensing device, the low material and fabrication costs, joined to chemical selectivity achieved without using any specific chemical label, might make these easily readable sensors viable for high technological readiness level devices. Moreover, the irreversible nature of the PPO phase transition allows label-free selectivity even to vapor of molecules with very similar structure.

5.8. Selectivity Mechanism

To better illustrate the phenomena occurring within the DBR, Figure 5.12 schematizes the processes inducing the behavior illustrated in Figure 5.9 and Figure 5.11. When the DBR is exposed to VOC vapors (A), the analyte penetrates within the structure starting from the layer contacting the environment and inducing the swelling and the crystallization of the amorphous PPO top layers (B in Figure 5.12 and Figure 5.8). The different degree of swelling interrupts the DBR periodicity resulting in the coexistence of two stop-band, as observed in

Figure 5.9. At longer exposure time, the analyte penetrates within all the layers, causing the disappearance of the stop-band assigned to the unswollen structure and a further red-shift of the stop-band assigned to the swollen one (C in Figure 5.12 and +” marks in Figure 5.9 a”- d”). Once the VOC vapors are removed from the environment, the guest is desorbed, and the PPO thin films retain a nanoporous crystalline phase with different density, thickness and optical properties than the initial amorphous phase. Indeed, the DBR stop-band have different spectral position and intensity than the starting samples containing the amorphous phase (Figure 5.11). The different kinetics of this process for the analyzed VOC vapors, together with the different spectral shift induced by the analyte generate the fingerprint response typical of the investigated molecule.

Figure 5.12: Schematic of the formation of PPO-VOC co-crystals within the DBR during vapor exposure (A, B) and of the guest desorption (C).

Table 5.1 summarizes the characteristics of the sensor and compare them with those of photonic crystal sensors recently reported in literature. Beside the mechanisms allowing selectivity, the table also focuses on fabrication processes, transduction methods and low detection limit, already discussed in Paragraphs 1.3 and 2.3.

We can distinguish three main selectivity mechanisms. The first includes devices based on arrays of labels, which provide selectivity through chemiometric analyses,¹⁰⁻¹⁴ or on more complicated optical techniques such as fluorimetry.^{13, 15, 16} As discussed in Paragraph 2.3, these labelled systems suffer of complicated signal transduction methods.

The second mechanism is based on the spectral shift of the stop-band induced by the variation of either the effective refractive index¹⁷⁻²⁵ or the optical thickness of the photonic crystal.^{10, 26, 27} Due to the similarity of VOC refractive indexes in the vapour phase, these systems suffer from three drawbacks. First, to allow detectable responses, the analyte must condensate within the photonic crystal porosity. Second, being the response of the system related to its effective refractive index, which in turn is a function of the volume fraction of the photonic crystal components, the void volume must be maximized, still allowing capillary condensation. Third, disentangling analytes having different refractive index could be complicate within specific concentration ranges. Indeed, low analyte concentrations may not allow significant optical variations.²² Moreover, low concentrations of an analyte with high refractive index induces the same optical changes of large concentrations of another analyte having a lower refractive index value.²⁸ The chemical selectivity of these system can be improved by including a size-selective materials such as a zeolite thin films in the photonic crystal,²⁴ by analyzing the combined response of two or more DBR having different porosity or periodicity,^{29, 30} or by introducing different variables (e.g. temperature) during the sensing process.³¹ These approaches enhance the selectivity but make the signal transduction more complicated.

The last selectivity mechanism reported is the one used in the present work, and is based on the different chemical and physical affinity between the photonic crystal components and the analytes. For instance, the response kinetics can be modified by introducing free volume within a polymer DBR, like for the nanocomposite sensors reported in Chapter 4. These differences allow diverse permeation kinetics which, together with the spectral shift induced by the analyte provide selectivity. In this case, the permeation kinetics and the stop-band spectral shift are induced by a variety of parameters including the analyte molecular size, the chemical affinity between the analyte and the polymer media, the media free volume, eventual phase transitions, and many others. Beside the present work, this mechanism has been reported only few times. The first example is represented by a SiO₂ opals infiltrated with a poly(ethylene glycol) methacrylate (PEGMA) gel swollen with ethylene glycol (EG).³² Here, the analyte can diffuse into the gel or extract the glycol with different kinetics depending on its polarity, viscosity and chemical affinity. In another case, three porous silicon lattices stacked one on the other, and having different porosity, allow different permeation kinetics of the analytes.³⁰ This mechanism offers unique responses to pure analytes, which are obtained by a simple reflectance or transmittance measurement collected at a determined exposure time. Thanks to the strong optical response typical of polymer DBR, this mechanism allows to recognize the analyte by simple naked eye investigation (Figure 5.9), offering the simplest selective signal transduction reported so far. In principle, the different affinity and diffusion kinetics of the analytes within the phase-changing PPO layers might also allow to identify a single vapor analyte within a complex mixture of vapors using a proper library of dynamic optical responses, but the analysis of mixture is still an open issue in the field of chromatic sensors based on DBRs”

Table 5.1: Characteristics of photonic crystal based VOC sensors.

Materials	Fabrication Method	Transduction Method	Detection limit	Selectivity mechanism	Number of analytes	Reversibility	Ref.
3D structures							
A PMMA -Cellulose	Self-assembly and infiltration	$\Delta\lambda$	10^1 ppm	$\Delta(n-d)$	4	Not Investigated	10
PMMA	E-beam lithography	MVA	10^1 ppm	silane labels (2)	5	Yes	11
SiO ₂	Self-assembly	$\Delta\lambda$	P ₀	Δn	2	Yes	17
SiO ₂	Self-assembly	MVA	10^2 ppm	silane labels (16)	8	Yes	12
SiO ₂	Self-assembly	Fluorimetry (CIA + MVA)	10^3 P ₀	emitting labels (7)	8	Yes	15
SiO ₂	Self-assembly and infiltration	$\Delta\lambda$	10^3 ppm	Δn	2	Yes	18
— TiO ₂ -MOF	Spin-coating and annealing	CIA	10^{-1} P ₀	Different MOFs (3)	2	Yes	29
MOF	Self-assembly and infiltration	$\Delta\lambda$	10^1 ppm	Δn	6	Yes	20
SiO ₂	Self-assembly, infiltration and calcination	Fluorimetry	10^3 mg/m ³	Not investigated	1	Yes	16
MOF	Self-assembly	$\Delta\lambda$	Not Investigated	Δn	7	Yes	19
H SiO ₂ -PEGMA-EG	Self-assembly, infiltration and calcination	Dynamic R/T	Not Investigated	Molecular interaction	32	Not Investigated	32
1D structures							
PS-PMMA	Spin-coating and UV curing	$\Delta\lambda$	Not Investigated	Not Investigated	1	Not Investigated	33
PTFE like - Au nanoparticles at PTFE like	Ion sputtering	$\Delta\lambda$	0.05 P ₀	$\Delta(n-d)$	3	Yes	26 27
PS-CA	Spin-coating	Dynamic R/T	10^1 ppm	Not Investigated	1	Not Investigated	This work
PPO-CA	Spin-coating	Dynamic R/T	10^1 ppm	Molecular interaction / phase transition	4	No	
Porous Silicon	Electrochemical etching	$\Delta\lambda$	10^2 ppm	silane labels (7)	2	Yes	13
Porous Silicon	Electrochemical etching	$\Delta\lambda$	<1 torr	Δn at different temperature	3	Yes	31
Porous Silicon	Electrochemical etching	Dynamic R/T	10^2 ppm	Δn in stacked DBRs with decreasing porosity	7	Yes	30
SiO ₂ -Activated Carbon	Electrochemical etching	$\Delta\lambda$	10^1 ppm	Δn	4	Yes	21
SiO ₂ -TiO ₂	Spin-coating and annealing	CIA	Not Investigated	silane labels (9)	6	Yes	14
SiO ₂ -TiO ₂	Spin-coating and annealing	$\Delta\lambda$	10^{-2} P ₀	Δn	1	Not Investigated	22
— SiO ₂ -TiO ₂	Spin-coating and annealing	$\Delta\lambda$	Not Investigated	Δn	4	Yes	23
SiO ₂ -TiO ₂	Spin-coating and annealing	$\Delta\lambda$	10^1 ppm	Not Investigated	1	Yes	36
SiO ₂ -TiO ₂ -Zeolite	Spin-coating and annealing	$\Delta\lambda$	10^{-1} P ₀	Not Investigated	1	Not Investigated	37
TiO ₂ -Zeolite	Spin-coating and annealing	$\Delta\lambda$	10^{-1} P ₀	Δn - Zeolite cage size section	4	Not Investigated	24
Nb ₂ O ₅ -Zeolite	Spin-coating and annealing	$\Delta\lambda$	10^2 ppm	Not Investigated	1	Yes	38
TiO ₂ -mixed metal oxides	Spin-coating and annealing	$\Delta\lambda$	Not Investigated	Δn	4	Yes	25
H V ₂ O ₅ - PMMA	Spin-coating	$\Delta\lambda$	Not Investigated	V ₂ O ₅ Δn - PMMA $\Delta(n-d)$	2	Not Investigated	39

P=polymer, I=inorganic, H=hybrid polymer-inorganic, MVA=Multivariate analysis, CIA=Color imagery analysis, MOF=Metal-organic framework,

R/T= Reflectance or transmittance spectroscopy, Δn =refractive index variation, $\Delta(n-d)$ =Optical thickness variation, $\Delta\lambda$ = stop-band wavelength variation

5.9. Outcomes

In this part of the project, the optical response of nanocomposite and clathrate DBR sensors to four aromatic homologues and carbon tetrachloride were compared. While the nanocomposite DBR was proven capable of disentangling VOC with different structures, only minor differences between its response to toluene and benzene were evinced. In contrast, when using poly(p-phenylene oxide) as the active material in DBR sensors, the formation of PPO-VOC co-crystalline phases enables selectivity to the four different molecules. The phase transition from amorphous to co-crystals was proven independently by comparing infrared measurements and ellipsometric data, and it was visible in the reflectance spectra of the sensors 24 h after exposure

5.10. References

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Chapter 6

Discussion and Future Work

This Thesis demonstrates new concept distributed Bragg reflector sensors for the detection of volatile organic compounds vapors. The new sensors are based on the interaction between the vapor molecules and all polymer Bragg multilayers whose sensitivity has been increased embedding permeable active media. The devices show label-free selectivity among aromatic homologues and carbon tetrachloride. As summarized in this Chapter, these characteristics, together with the low fabrication costs and ease of signal transduction promises new lab-on-a-chip devices for the extensive monitoring of air quality.

These results pave the way to the development of polymer distributed Bragg reflector for selective detection of hazardous gases and to further simplify the fabrication process embedding the active media into commercial polymer and inorganic dichroic filters.

This work also allowed parallel projects which have not been reported in this Thesis for consistency and are summarized in the last Paragraph of this Chapter.

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6.1. Outcomes

Chapter 1 and 2 report the advantages related to the use of polymer DBRs for sensing purpose. These structures were promising to allow simpler and faster analyses than established methods for VOC detection, to reduce the cost of fabrication, and to simplify the signal transduction of colorimetric vapor sensors. On the other hand, the lack of selectivity and the low sensitivity of polymer DBRs was hindering their use. The next Paragraphs summarize the approaches used to overcome these issues and the achievements accomplished during the project.

6.1.1. Enhanced Sensitivity

The low sensitivity of polymer DBR sensors is related to the low vapor permeability offered by amorphous polymers. This limitation was successfully overcome introducing permeable sensing regions within standard polymer DBRs in the form of hybrid polymer-inorganic nanocomposite and of phase-changing poly(p-phenylene oxide).

The nanocomposite DBR sensors were realized alternating layers of cellulose acetate as low index medium and polystyrene matrices loaded with ZnO nanoparticles. To develop these sensors, nanocomposite thin films were fabricated by spin coating of the ZnO nanoparticle dispersion into polystyrene-toluene solution. The loading allows increasing the permeability of the matrix by 3.5 times, yet maintaining the transparency of the system. By implementing the nanocomposite into DBRs, sensitivity to toluene vapor below 1 ppm, with response time of the order of few seconds were achieved.

The sensitivity achieved with PPO DBR sensors exploits instead the capability of this polymer to intake a large amount of guest molecule and to undergo a phase transition. This results were achieved by a systematic study of the deposition condition allowing the formation of thin films in the amorphous phase.

6.1.2. Label-Free Selectivity

This project demonstrates polymer DBR vapor sensors capable of label-free selectivity among VOC vapors for the first time.

The nanocomposite sensors show different optical behavior to environments rich in benzene, ortho dichlorobenzene and carbon tetrachloride, but cannot distinguish among molecules with very similar structures such as benzene and toluene. The selectivity limits of nanocomposite DBRs were overcome using phase-changing poly (p-phenilenoxide) as active sensing material. The capability to obtain good optical quality thin films and DBRs containing both the amorphous and the semi-crystalline PPO phase was demonstrated. The amorphous PPO was tested as active medium in DBR sensors together with cellulose acetate, showing full selectivity among toluene, benzene, carbon tetrachloride and ortho dichlorobenzene. Infrared investigation confirmed that vapor exposure induces a phase transition in the PPO film. In turn, the formation of different PPO co-crystals allows engineering different optical responses of the sensor to different analytes.

6.1.3. Simple Fabrication

Chapters 1 and 2 explain the complicated procedure necessary to achieve a selective and sensitive assessment of VOC pollutants. While standard techniques require costly and time consuming sampling, analyte separation and detection, the most diffuse colorimetric devices necessitate labelling with chemical targets, complicated signal transductions and fabrication procedures.

This Thesis demonstrates selective DBR sensors fabricated with faster, simpler and cheaper procedures than any other reported so far. All the devices were fabricated by spin-coating of polymer solution and did not require any chemical labelling to achieve selectivity or thermal treatment to provide mechanical stability to the structure.

6.1.4. Easy Signal Transduciton and Portable Devices

DBR response detectable by naked eyes and without instrumentation was demonstrated. Nevertheless, if higher sensitivity is required, DBR sensors can also be coupled to a spectrometer. The use of completely fiberized optical setups for full characterization of sensing performance was demonstrated. Thus, even high sensitivity colorimetric sensing using the platform described in this Thesis would only require carrying a spectrometer and light source that may be integrated in a compact, handheld instrument, thus simplifying significantly current measurement procedures required for VOC sensing. Development of a “turn-key” compact measuring system could be the subject of future translational research in academia and industry. The capability to assess the DBRs optical response in polluted environment by naked eyes, will allow un-trained operators to evaluate endangering atmosphere without the use of specific equipment.

6.2. Perspectives of the Project

The results reported in this Thesis open a new research path for the use of all-polymer DBRs for the fast and selective detection of vapors. This paragraph focuses on the short-term challenges to device development, and proposes other active systems for the sensing of different families of compounds.

6.2.1. Short-Term Challenges

This project demonstrates nanocomposite sensors with sensitivity of 0.5 ppm, lower detection limit of ~20 ppm and response time below 1 min. While these devices show selectivity only among molecules with very different structure (see Chapter 4), sensors based on the phase transition of PPO thin films show better selectivity, together with response time of few minutes, and comparable detection

limit and sensitivity (see Chapter 5). These achievements represent the starting point for devices development, and provide the benchmarks for this project. In view of industrial applications, the next steps will focus on the capability to operate the sensors within a wide range of temperatures, to disentangle analytes within complex mixtures of vapors, and to improve the detection limit.

Temperature can indeed affect the analyte concentration, the diffusion processes, and the polymer chain mobility. Consequently, definition of a range of operational temperatures will be critical to develop sensors for both industrial and urban applications.

Concerning the analysis of complex mixtures, it can currently be accomplished only by standard chromatographic techniques using a library of references (see Paragraph 2.1). This task will require to build a library of responses for both pure analytes and mixtures. To tackle this problem, the optical response of DBR sensors to binary mixtures is currently under investigation.

Last, as mentioned in Paragraph 1.1, many VOC are toxic even in concentration below 1 ppm. The high toxicity of these pollutants makes the detection limit of the sensors critical for applications in industrial plants. As mentioned above, this Thesis demonstrates sensors responsive to few dozens of parts per million. Such value is comparable with state of the art sensors (See Table 5.1). On the other hand, the assessment of the sensor responses to lower concentrations, will require strong vapor dilutions, and a tight concentration control.

To investigate the effects of temperature, the response to complex mixtures, and the lower detection limit of the sensors, a set-up that combine temperature control, gas flow enrichment and dilution lines is currently in phase of design.

6.2.2. DBRs for Molecular Gas Detection

All polymer DBRs can also be potentially used to detect hazardous gases in residential and industrial environments, where leakage of odor-less gases, like

carbon monoxide can seriously affect people's health.

In 2012, G. Guerra and co-workers demonstrated different permeability of amorphous and nanoporous semi-crystalline PPO to different gases.¹ The crystalline PPO phase was obtained by intercalation of benzene and carbon tetrachloride into the PPO matrix and their extraction in supercritical CO_2 . Such treatment does not affect the crystalline phase, which is characterized by porosity with size comparable to the guest molecule volume. Figure 6.1 shows the diffusivity of methane (a), carbon dioxide (b), propane (c) and benzene (d) within amorphous PPO (●) and nanoporous semi-crystalline PPO fabricated by extraction of benzene (■) and carbon tetrachloride (▲). In the four cases, the three PPO phases allow different diffusivity of the gases. Indeed, the nano-crystalline PPO fabricated by carbon tetrachloride showed higher molecular diffusivity, followed by the one fabricated from benzene and the amorphous.

Figure 6.1: Diffusivity isotherms at 30 °C for (a) CH₄, (b) CO₂, (c) C₃H₈, and (d) C₃H₆ in aPPO (●), bPPO (■), and cPPO (▲).¹

Selective adsorption of the nanoporous semi-crystalline PPO phase of gases with different diffusivity could be exploited to achieve colorimetric detectors to monitor carbon monoxide and methane. If successful, the simple colorimetric response of the device would allow the public to constantly monitor vapor leakages in households. For this purpose, one should test formation of the nanoporous semi-crystalline PPO phase within spun-cast all polymer DBRs. The DBR sensor shall then be exposed to vapor of molecules to induce the amorphous to crystalline transition without affecting the optical quality of the photonic lattice, and its optical response to environments rich in molecular gases shall be characterized and calibrated.

6.2.3. Coupling Non-Sensitive DBRs with Permeable Capping Layers

Manufacturing of polymer DBR sensors can be further simplified while maintaining the characteristic sensitivity. Chapter 4 and 5 show that the optical response of the sensors can be based on the sole swelling of the DBR capping layer. Indeed, the penetration of the vapors within this single thin film allows well detectable shifts of the stop-band position.

Based on these preliminary findings, a future research path could deal with the coupling of standard unresponsive DBRs with highly permeable capping layers able to absorb large number of analytes. This would allow strong spectral variation with standard lattices, which require simpler and faster fabrication procedures. As a proof of principle, Figure 6.2 compares the response of a 10+1 PS-CA period DBR with polystyrene capping layer (Figure 6.2 a) and nanocomposite capping layer (Figure 6.2 b) to toluene vapor. As expected, when the capping layer is polystyrene, the stop-band, visible in red tones, undergoes slightly detectable variation. On the other hand, when the capping layer is the permeable nanocomposite, both stop-band intensity and spectral position vary. Indeed, the peak position red shifts by ~40 nm, from 690 nm to 730 nm, within 10 minutes. These preliminary results suggest the possibility to achieve fast

detection of molecules coupling standard DBRs with a variety of permeable polymers which usually do not have sufficient optical quality to be incorporated into DBR.

Figure 6.2: Dynamic spectral response to 120 ppm of toluene vapors of a) PS-CA DBR, and b) the same sample where the last layer is loaded with ZnO nanoparticles.

This approach will also allow the use of commercial inorganic DBRs as reusable sensors, and the enhancement of the response of porous structures. As a proof of principle, Figure 6.3 reports the simulated optical response of a 4+1 periods DBR made of TiO_2 and SiO_2 with a polymer capping layer made of 120 nm thick nanocomposite. The spectrum of Figure 6.3 a shows the calculated DBR transmission with minimum centered at ~620 nm. Figure 6.3 b shows the evolution of the spectra simulated for the DBR with capping layer of increasing thickness, in the range of intensity highlighted by the gray panel in Figure 6.3 a. The contour-plot shows that the swelling of the nanocomposite layer induces a variation of the stop-band shape, consisting in the splitting into the two structures already seen for polymer sensors.

Figure 6.3: a) Calculated spectrum of a $\text{TiO}_2\text{-SiO}_2$ DBR with a 120 nm thick capping layer made of nanocomposite. b) Dynamic spectral response to the swelling of the capping layer.

This approach is also promising for the eventual manufacturing scale-up, by combining large-area polymer DBRs fabricated industrially (Figure 6.4) with single layer active materials.

Together with the study of new active media, the DBR sensing platforms could be implement into devices

Figure 6.4: a) Large area DBR fabricated by layer-by-layer spray deposition.² b) Commercially available 3M dichroic mirror.³

6.3. Related Projects

This work allowed parallel projects, which have not been reported in this Thesis for consistency, but led to several conference communications and two manuscripts in preparation (See Conference Contributions -3, 4, 9, 17- and List of Publications -3, 4-).

This project demonstrated that DBRs with low dielectric contrast are advantageous for sensing purposes. On the other hand, the low dielectric contrast within polymer structures usually does not allow applications requiring strong coupling and Purcell effect. However, mechanical flexibility and simple fabrication processes make them very attractive for light management applications including directional spectral redistribution of photoluminescence and optical switching. The compatibility with solution based fabrication techniques, and easily tunable optoelectronic properties by simple compositional design make perovskite structures interesting for these purposes. Indeed, beside serving as efficient photovoltaic materials,⁴⁻⁸ perovskites are gaining increasing interest due to their potential as light emitters.⁹⁻¹² Among them, broadband white emitting structures¹³ are promising for new concept perovskite-based lighting devices.

This project demonstrated single color suppression and enhancement of white emitting thin films of EDBE PbCl₄ perovskite¹³ embedded in DBR structures (Figure 6.5 a). When coupled with the DBR, the perovskite emission profile (red line of Figure 6.5 b) undergoes single color suppression (green line) or enhancement (blue line) in correspondence of the stop-band wavelength depending on the use of the DBR as a filter or as a mirror. Photonic structures where the perovskite emitter was placed in microcavities allowing localized emission enhancement of a factor ~1.5 were also fabricated. The microcavities demonstrated low quality factor due to polymer-perovskite low mutual processability. Indeed, the spin-coating method requires reciprocal insolubility of polymer-solvent and emitter-solvent pairs to avoid dissolution of the

underlying layers and thus disorder and light scattering. Perovskites can be solubilized and spun-cast only by highly complexing, broad spectrum solvents like dimethyl sulfoxide and dimethylformamide,¹⁴⁻¹⁶ which are also capable of dissolving majority of the polymers.¹⁷ Therefore, different approaches to protect the underlying DBR from dissolution, but maintaining a full solution based fabrication process are currently being tested.

Figure 6.5: a) From left to right: polymer-EDBE PbCl_4 DBR schematization, photographs of perovskite-DBRs with stop-band at different wavelength and a free-standing polymer DBR. b) EDBE PbCl_4 thin film absorbance (black line) and emission spectra of bare perovskite (red line) and coupling the perovskite with a DBR filter (green line) and mirror (blue line).

Light management was also the focus of another project carried out during my first years of candidature, and aimed to develop antireflective surfaces for photovoltaic applications via metal assisted chemical etching.

The growing demand for renewable energy generation is making performance enhancement critical for photovoltaic technologies. Hybrid tandem systems, where inorganic semiconductors are coupled with photoactive materials to extend the absorption spectrum, promise a viable approach to achieve efficiencies higher than the Shockley–Queisser limit.¹⁸⁻²⁰ On the other hand, when photoactive materials with high recombination rate are used to extend the spectrum, the devices often suffer from radiative losses, which hinder high power conversion efficiencies. These losses can be reduced recycling the emitted photons.²¹⁻²³ In this regard, wet processes for the fabrication of light trapping surface in inorganic semiconductors are arising increasing interest.

In this part of my PhD work, I demonstrate a lithography-free gold catalyzed etching mechanism for the fabrication of near zero reflection GaAs (black GaAs). Thanks to its high electron mobility and absorption coefficient,²⁴ GaAs is one of the most promising semiconductor, and it has already been demonstrated as an excellent electron acceptor and hole donor in combination with photoactive polymers.²⁵⁻²⁹

The new surface is fabricated by electroless deposition of gold nanoparticles and etching in H_2O_2 and HF. As an example, Figure 6.6 a reports the SEM micrograph of etched GaAs (111) B surface characterized by faceted hillocks. Cross sectional micrographs were used to identify GaAs crystallographic planes undergoing slow etching rate (corresponding to the feature slopes) by comparison with a representation of the GaAs crystal structure (Figure 6.6 b), and to simulate the geometrical light trapping occurring within the surface (Figure 6.6 c). Reflectance measurements show that the reflectance of the polished surface (red line of Figure 6.6 d) undergoes 50 folds decrease after the etching process. The new systems were proven to induce reabsorption of emitted photons when coupled with poly (3-hexylthiophene).

Figure 6.6: a) Tilted scanning electron microscopy micrographs of etched (111) B GaAs. b) Comparison between the etched surface geometry with the GaAs crystal representation. c) Ray tracing light trapping simulation within the GaAs surface. d) Normal incidence reflectance of polished (red line) and etched (blue line) (111) B GaAs surfaces.

The studies on all-polymer and hybrid photonic crystals for sensing and light management will also be the focus of my future research project within the Horizon 2020 Marie Skłodowska-Curie action Synchronics (Supramolecularly eNginEered arCHitectures for opROelectronics and PhotonICS).³⁰ The project unifies twelve international teams including universities and companies and aims to develop novel and more performing supramolecular materials and structures for photonic applications that can be manufactured cheaply. In this project, I will

continue the work on sensing devices and focus on the implementation of new photoactive materials including perovskites, J-aggregates, conjugated polymers and photochromic systems in polymer photonic structures. For this purpose, I will focus on new strategies to overcome processability issues and to increase the dielectric contrast within polymer photonic crystal.

6.4. References

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List of Publications

- 1 P. Lova, C. Bastianini, P. Giusto, M. Patrini, P. Rizzo, G. Guerra, M. Iodice, C. Soci, and D. Comoretto. *Label-Free Vapor Selectivity in Poly(p-phenylene Oxide) Photonic Crystals Sensors*. ACS Applied Materials & Interfaces, 2, 31941, 2016. **(Corresponding Author)**
- 2 P. Lova and C. Soci. *Organic and hybrid photonic crystals*; Chapter 9: *Nanoimprint lithography: toward functional photonic crystals*. Edited by Springer. 2015. **(Corresponding Author)**
- 3 P. Lova, G. Manfredi, L. Boarino, A. Comite, M. Laus, M. Patrini, C. Soci and D. Comoretto. *Polymer distributed Bragg reflectors for vapor sensing*. ACS Photonics, 2, 537, 2015. **(Corresponding Author)**
- 4 P. Lova, G. Manfredi, L. Boarino, M. Laus, G. Urbinati, T. Losco, F. Marabelli, V. Caratto, M. Ferretti, M. Castellano, C. Soci and D. Comoretto. *Hybrid ZnO: polystyrene nanocomposite for all-polymer photonic crystals*. Phys. Status Solidi C, 12, 158, 2014.
- 5 J. Yin, D. B. Migas, M. Panahandeh-Fard, S. Chen, Z. Wang, P. Lova and C. Soci. *Charge redistribution at GaAs/P3HT heterointerfaces with different surface polarity*. J. Phys. Chem. Lett., 4, 3303, 2013.

In preparation:

- 6 P. Lova, D. Cortecchia, C. Bastianini, H.N. Swaha Krishnamoorthy, A. Bruno, D. Comoretto, C. Soci. *Directional control of EDBE PbCl₄ perovskite photoluminescence*.
- 7 P. Lova, V. Robbiano, F. Cacialli, D. Comoretto, C. Soci. *Metal assisted chemical etching for highly performing GaAs antireflective surfaces*.
- 8 M. Kumar, A. Bruno, P. Lova, L. Yeghiazaryan, G. Gurzadyan, C. Soci. *Multiple exciton generation in low dimensional PbSe nanostructures*

Conference Contributions

1. EOSAM 2016 - European Optical Society Annual Meeting 2016, 26-30 September 2016, Berlin, Germany
 - ✓ P. Lova, V. Grande, S. Herbst, F. Würthner, and D. Comoretto. *Perylene Bisimide J-Aggregates All-Polymer Microcavities*. (**Poster, Presenting**)
 - ✓ P. Lova, C. Bastianini, M. Patrini, P. Rizzo, G. Guerra, M. Iodice, C. Soci and D. Comoretto. *Label-Free Vapor Selectivity in Poly(p-phenylene oxide) Photonic Crystal Sensors*. (**Poster**)
2. AIM 2016 - XXII Convegno Nazionale dell'Associazione Italiana di Scienza e Tecnologia delle Macromolecole, 11-14 September 2016 Genova, Italy.
 - ✓ P. Lova, V. Grande, S. Herbst, F. Würthner, and D. Comoretto. *Perylene Bisimide J-Aggregates All-Polymer Microcavity*. (**Poster, Presenting**)
 - ✓ P. Lova, C. Bastianini, M. Patrini, P. Rizzo, G. Guerra, M. Iodice, C. Soci, D. Comoretto. *Sensori Fotonici Senza Recettori a Base di Polifenilenossido per l'Analisi Qualitativa di Vapori Organici*. (**Oral, Presenting**)
 - ✓ P. Giusto, C. Bastianini, P. Lova and D. Comoretto. *I Colori dei Cristalli Fotonici*. (**Poster**)
3. GISR 2016 - Italian Meeting on Raman Spectroscopies and Non-Linear Optical Effects, 14-16 September 2016, Padova, Italy.
 - ✓ D. Comoretto, G. Manfredi, P. Giusto, P. Lova, L. Fornasari, F. Floris, M. Patrini, F. Marabelli. *Spectral Redistribution of Fluorescence Intensity in All-Polymer Microcavities and Distributed Bragg Reflectors*. (**Oral**)
4. HOPV 2016 - International Conference on Hybrid and Organic Photovoltaics, 28 June – 1 July 2016, Swansea, United Kingdom
 - ✓ D. Cortecchia, Y. Jun, P. Lova, S. Mhaisalkar, G. Gurzadyan, A. Bruno, C. Soci. *Role of Polaronic Excitons in White-light Emitting Hybrid Perovskites* (**Oral**)
5. EUPOC 2016 – Europolymer Conference 2016, 22-26 May 2016, Gargano,

Italy.

- ✓ C. Bastianini, P. Lova, A. Servida, D. Comoretto. *All-polymer Optical Sensors for Alcohols Detection*. **(Poster)**
- ✓ P. Lova, C. Bastianini, M. Patrini, P. Rizzo, G. Guerra, M. Iodice, C. Soci, D. Comoretto *Label-free Selectivity in Polymer Photonic Crystals Sensors*. **(Poster, Presenting)**
- 6. IPS 2016 - Institute of Physics Singapore Meeting 2014, 7-8 March 2016, Singapore.
- ✓ M. D. Birowosuto, D. Cortecchia, K. C. Lew, P. Lova, A. Bruno and C. Soci. *Plasmonic Enhancement of Spontaneous Emission in Metal-Perovskite Slabs*. **(Poster)**
- ✓ K. C. Lew, D. Cortecchia, C. Xin Yu, P. Lova, A. Bruno, C. Soci. *Hybrid Organic-Inorganic Perovskite Nanostructures*. **(Poster)**
- 7. PSCO 2015 - 1st International Conference on Perovskite Solar Cells and Optoelectronics, 27-29 Sep 2015, Lausanne, Switzerland
- ✓ P. Lova, D. Cortecchia, C. Bastianini, H.N.S. Krishnamoorthy, D. Comoretto, A. Bruno, C. Soci. *Solution Processable Perovskite-Polymer Microcavities*. **(Poster)**.
- ✓ D. Cortecchia, Z. Wang, M.J. Young, J. Yin, C. Shi, P. Lova, G. Gurzadyan, A. Bruno, S. Mhaisalkar, C. Soci. *(EDBE) PbX₄ Perovskite White Emitting Devices*. **(Poster)**.
- 8. ICMAT 2015 - International Conference on Materials for Advanced Technologies, Singapore, 28 Jun - 3 Jul 2015:
- ✓ M. Kumar, A. Bruno, J. Yin, Z. Wang, P. Lova, G.G. Gurzadyan, C. Soci. *Multiple Exciton Generation in Low-Dimensional PbSe Nanostructures*. **(Poster)**.
- 9. 15th European Polymer Federation Congress, 21-26 Jun 2015, Dresden, Germany
- ✓ P. Lova, M. Patrini, F. Marabelli, G. Guizzetti, G. Manfredi, A. Comite, M. Laus, L. Boarino, G. Ianniello, P. Rizzo, C. Daniel, G. Guerra, C. Soci, D.

- Comoretto. *Vapor Sensing by All-Polymer 1D Planar Photonic Crystals*. **(Oral)**.
10. E-MRS 2015 S.M. - European Material Research Society Spring Meeting 2015: 26-30 May 2015, Lille, France.
- ✓ P. Lova, M. Patrini, F. Marabelli, G. Manfredi, A. Comite, M. Laus, L. Boarino, G. Ianniello, P. Rizzo, C. Daniel G. Guerra C. Soci, D. Comoretto. *Polymer Photonic Crystal Vapor Sensors*. **(Oral)**.
- ✓ Kumar, A. Bruno, J. Yin, P. Lova, Z. Wang, G. Gurzadyan, C. Soci. *Dimensionality Effects on Multiple Exciton Generation in PbSe Nanostructures*. **(Oral)**.
11. Fourth International Symposium Frontiers in Polymer Science, 20-22 May 2015, Riva del Garda, Italy
- ✓ E. Bozzoni, S. Congiu, S. Gazzo, R. Knarr, F. La Rosa, G. Manfredi, D. Comoretto P. Lova, C. Soci, G. Ianniello, P. Rizzo, C. Daniel, G. Guerra, E. Martinelli, G. Galli, K. Sparnacci, M. Laus, L. Boarino, M. Lanzi, G. Zuccheri. *Polymer Photonic Crystal Structures*. **(Poster)**.
12. MRS 2015 S.M. - Material Research Society Spring Meeting 2015, 6-10 Apr 2015, San Francisco, U.S.A.
- ✓ P. Lova, V. Robbiano, A. Bruno, F. Cacialli, D. Comoretto, C. Soci. *Black GaAs*. **(Oral, Presenting)**.
- ✓ P. Lova, G. Manfredi, L. Boarino, A. Comite, M. Laus, M. Patrini, F. Marabelli, C. Soci, D. Comoretto. *Vapor Sensing by 1D-Polymer Photonic Crystal*. **(Oral, Presenting)**.
- ✓ M. Kumar, A. Bruno, P. Lova, L. Yeghiazaryan, G. Gurzadyan, C. Soci. *Multiple Exciton Generation (MEG) in Low Dimensional PbSe Nanostructures*. **(Poster, Presenting)**.
13. IPS 2015 - Institute of Physics Singapore Meeting 2015, 4-6 Mar 2015, Singapore.
- ✓ P. Lova, G. Manfredi, A. Bruno, D. Comoretto and C. Soci. *Polymer Photonic Crystals Vapor Sensors*. **(Oral, Presenting)**.

- ✓ M. Kumar, A. Bruno, A. Chaturvedi, J. Yin, P. Lova, Z. Wang, G. Gurzadyan, C. Soci. *Carrier Multiplication in Low Dimensional PbSe Nanostructures*. (**Poster**).
- 14. JAPAN-SINGAPORE WORKSHOP on Nanophotonics, Plasmonics, and Metamaterials, 11-12 Dec 2014, Singapore
- ✓ P. Lova, Z. Wang, D. Comoretto, C. Soci. *Polymer Distributed Bragg Reflectors for Vapor Sensing*. (**Poster, Presenting**).
- 15. Workshop on Recent Advances and New Perspective in Polymer Crystallization, 29-30 Sep 2014, Genova, Italy
- ✓ E. Bozzoni, G. Manfredi, S. Gazzo, D. Comoretto, P. Lova, C. Soci, E. Di Gaetano, M. Patrini, G. Guizzetti, G. Ianniello, P. Rizzo, C. Daniel, G. Guerra. *Nanoporous Crystalline and Amorphous Poly (Phenylene-Oxide) For All-Polymer Photonic Crystal Sensors*. (**Poster, presenting**).
- 16. POLYSOLVAT 10 - International IUPAC Conference Polymer-Solvent Complexes & Intercalates, 22-25 Sep 2014, Salerno, Italy
- ✓ E. Bozzoni, G. Manfredi, S. Gazzo, D. Comoretto, P. Lova, C. Soci, E. Di Gaetano, M. Patrini, G. Guizzetti, G. Ianniello, *Poly (Phenylene-Oxide) Clathrates for All-Polymer Photonic Crystal Sensors*. (**Oral**).
- 17. NANOFORUM 2014, 22-25 Sep 2014, Rome, Italy.
- ✓ P. Lova. *All-Polymer Nanostructures for Photonics*. (**Invited oral, Presenting**).
- 18. EOSAM 2014 - European Optical Society Annual Meeting 2014, 15-19 Sep 2014, Berlin, Germany.
- ✓ P. Lova, G. Manfredi, A. Comite, L. Boarino, M. Laus, M. Patrini, F. Marabelli, C. Soci, D. Comoretto. *Solvent Vapor Sensing by Hybrid Polymer-ZnO 1D Photonic Crystals*. (**Oral, Presenting**).
- 19. GISR 2014, III Italian Meeting on Raman Spectroscopy and Non- Linear Optical Effects, 9-11 Jun 2014, Parma, Italy

- ✓ P. Lova, G. Manfredi, L. Boarino, M. Laus, M. Patrini, F. Marabelli, C. Soci, D. Comoretto. *Optical Nanocomposite for Polymer Distributed Bragg Reflectors*. **(Poster)**.
- 20. E-MRS 2014 S. M. - European Material Research Society Spring Meeting 2014: 26-30 May 2014, Lille, France.
- ✓ P. Lova, G. Manfredi, L. Boarino, M. Laus, M. Patrini, F. Marabelli, C. Soci, D. Comoretto. *Photonic Crystal Vapor Sensors*. **(Poster, Presenting, awarded with Best Poster Prize)**.
- ✓ P. Lova, V. Robbiano, F. Cacialli, D. Comoretto, C. Soci. *Metal Assisted Chemical Etching of GaAs For Light Management in Photovoltaic Devices*. **(Oral, Presenting)**
- 21. META 2014 - The 5th International Conference on Metamaterials, Photonic Crystals and Metamaterials, 20-30 May 2014, Singapore.
- ✓ P. Lova, G. Manfredi, L. Boarino, M. Laus, G. Urbinati, T. Losco, F. Marabelli, V. Caratto, M. Ferretti, M. Castellano, C. Soci and D. Comoretto. *All-Polymer 1D Photonic Crystals*. **(Oral)**.
- 22. IPS 2014 - Institute of Physics Singapore Meeting 2014, 27-28 Feb 2014, Singapore.
- ✓ P. Lova, L. Boarino, M. Laus, F. Marabelli, C. Soci, D. Comoretto. *All-Polymer Distributed Bragg Reflectors*. **(Oral, Presenting)**.
- 23. ICMAT 2013 - The 7th International Conference on Materials for Advanced Technologies, 30 Jun-5 Jul 2013, Singapore.
- ✓ P. Lova, L. Boarino, D. Antonioli, M. Laus, G. Urbinati, F. Marabelli, C. Soci, and D. Comoretto. *Hybrid ZnO Nanocomposite - Polymer Distributed Bragg Reflectors*. **(Oral, Presenting)**.
- 24. ICSM 2014 - International Conference on Synthetic Metal, 30 Jun-5 Jul 2014, Turku, Finland
- ✓ P. Lova, G. Manfredi, L. Boarino, M. Laus, F. Marabelli, C. Soci, D. Comoretto. *Optical Nanocomposite for Polymer Distributed Bragg Reflectors Sensors*. **(Poster)**.

25. EOSAM 2012 - 4th European Optical Society Annual Meeting, 25-28 Sep 2012, Aberdeen, Great Britain
- ✓ P. Lova, L. Boarino, D. Antonioli, M. Laus, G. Urbinati, T. Losco, M.C. Ungureanu, V. Caratto, M. Ferretti, F. Marabelli, D. Comoretto. *Development of ZnO-Polystyrene Nanocomposite Suitable For The Preparation of Plastic Distributed Bragg Reflectors (DBR). (Poster).*
26. FUTURMAT 2 - Second International Meeting on Organic Materials for a Better Future, 16-20 Sep 2012, Brindisi, Italy.
- ✓ G. Canazza, F. Gagliardi, P. Lova, L. Occhi, S. Ottonello, V. Robbiano, S. Congiu, M. Alloisio, D. Comoretto. *Plastic Photonic Crystals: Fluorescence Enhancement in Conjugated Systems. (Poster).*