We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Fiber Optic Chemical Sensors based on Single-Walled Carbon Nanotubes: Perspectives and Challenges

Marco Consales¹, Antonello Cutolo¹, Michele Penza², Patrizia Aversa²,
Michele Giordano³ and Andrea Cusano¹

¹ *Optoelectronic Division, University of Sannio, Benevento, Italy*

² *Department of Physical Technologies and New Materials, ENEA, Brindisi, Italy*

³ *Institute for Composite and Biomedical Materials, CNR, Portici, Italy*

1. Introduction

Carbon nanotubes (CNTs) have become a highly-studied material class in recent years for numerous applications in nanoscience and nanotechnology due to their outstanding physical and chemical properties. High chemical reactivity, excellent mechanical strength but ultra-light weight, high thermal stability, high electron mobility, rich electronic properties, high aspect ratio, hollow nanostructure, large surface area make CNTs an ideal platform for many nanomaterial micro/nano-systems and process control practical applications. Conceptually, carbon nanotubes are viewed as rolled-up structures at nanoscale into seamless cylinders of single or multiple sheets of graphene to engineering single-walled and coaxial multi-walled carbon nanotubes, respectively. Generally, the diameter of a single nanotube ranges from 1 to 5 nanometers; while the bundles of roped multiple nanotubes have a diameter varying in the range of 5-100 nm. These one-dimensional nanostructured carbon allotropes have been applying to explore their potential in chemical gas sensing and biosensing.

This chapter reviews the development of high performance opto-chemical sensors based on the integration of CNTs with the optical fiber technology. The paper starts with an overview of the CNT amazing features and their exploitation as highly adsorbent nano-scale materials for chemical sensing. The attention is then focused on the operating principle, fabrication and characterization of fiber optic chemo-sensors in the Fabry-Perot type reflectometric configuration, realized by means of the deposition of a thin sensitive layer of single-walled carbon nanotubes (SWCNTs)-based material on the distal end of standard silica optical fibers (SOFs). This is followed by an extensive review of the excellent room temperature sensing capabilities of the realized SWCNT sensors against Volatile Organic Compounds (VOCs) in different environments (air and water). The experimental results here reported reveal that ppm and sub-ppm chemical detection limits, low response times as well as fast and complete recovery of the sensor responses have been obtained in most of the investigated cases. This evidences the great potentialities of the proposed photonic sensors

based on SWCNTs and their feasibility to be successfully employed for practical environmental monitoring applications, both in vapor or liquid phase. Furthermore, the use of SWCNT-based nanocomposites as novel sensitive fiber coatings is proposed to enhance the chemical sensing performance and improve the adhesion of CNTs to the fiber surface. It will also be shown how the typical poor selectivity of SWCNTs-based sensors towards a given chemical specie can be overcome by using standard pattern recognition techniques applied to fiber optic sensor arrays, exploiting both the static and dynamical features of the single sensor responses.

2. Chemical sensors for environmental monitoring

Environmental monitoring is required to protect the public and the environment from toxic contaminants and pathogens that can be released into a variety of media including air, soil, and water. Air pollutants include sulfur dioxide, carbon monoxide, nitrogen dioxide, and VOCs, which originate from sources such as vehicle emissions, power plants, refineries, and industrial and laboratory processes. Soil and water contaminants can be classified as microbiological, radioactive, inorganic, synthetic organic, and VOCs. Pesticide and herbicides are applied directly to plants and soils, and incidental releases of other contaminants can originate from spills, leaking pipes, underground storage tanks, waste dumps, and waste repositories. Some of these contaminants can persist for many years and migrate through large regions of soil until they reach water resources, where they may present an ecological or human-health threat. The current monitoring methods are mainly based on off-site laboratory analyses and are costly and time-consuming. In addition, limitations in sampling and analytical techniques occur (Wilson et al., 1995; Looney and Falta, 2000). For this reason, a need exists for accurate, inexpensive, continuous and long-term monitoring of environmental contaminants using sensors that can be operated on site.

Chemical sensors can be in most cases schematically described as composed of a sensitive part which, interacting with the surrounding environment, collects and concentrate molecules at or within the surface undergoing physical changes, and of an opportune transducer that converts into an interpretable and quantifiable term such modification of the sensing part. The heart of the chemical sensor is the sensitive element which is the interface between transducer and external environment so that the nature, the selectivity and sensitivity of the sensor depends upon these interactive materials. Good materials to use as sensing part should optimize specific interactions with a target analyte or narrow class of analytes, should provide a fast and reversible diffusion of the penetrants, small recovery times and should maintain the physical state so as the geometry over several cycles of use, in order to avoid hysteretic effects, and thus to ensure the reproducibility (Grate & Abram, 1991). Candidate materials for chemical sensors include polymers, organic monolayers, ceramics, metals semiconductors, nanostructured and porous materials (nanomaterials, molecular sieves, sol-gels, aerogels), biomolecules and combination thereof.

The natural step following the selective recognition of an analyte from the sensitive layer is the signal transduction, and thus the choice of an opportune technique to read the physical or chemical changes occurring at the sensing part. Transducing approaches can include mechanical (acoustic wave, micromechanical), electrochemical, optical, thermal, and electronic types. Each has strengths and weaknesses relative to the particular application.

Each transduction principle can be implemented in a variety of configurations, and fabricated by multiple approaches, resulting in many different sensing platforms.

A number of chemical sensors have been developed for environmental monitoring applications, a classification of which can be carried out upon their principal physics and operating mechanisms. The most exploited transduction principles in chemical sensing are the mass change and the resistivity/conductivity change of the sensitive element occurring on exposure to and consequent sorption of molecules of target environmental analytes. The first physical parameter is in many cases measured by the shift in the resonant frequency of an oscillating piezoelectric crystal. Depending on the kind of vibrational wave propagated in the crystal, a mass sensor can be classified as Quartz Crystal Microbalance (QCM) or Surface Acoustic Wave (SAW) sensor (Hartman et al., 1994; Kepley et al., 1992; Penza et al., 2006_a). They typically use a thin polymeric film as sensitive layer (Grate, 2000), however SAW and QCM-based chemical sensors using other sensitive coatings have been proposed (Zhang et al., 2004; Penza et al., 2005_a). Instead, resistivity/conductivity changes are typically detected by conductometric measurement carried out on sensitive materials (mainly semiconducting metal oxides and conjugated polymers) deposited between two electrodes. These sensor technologies carry the name of Metal Oxide Semiconductors (MOS) and Conductive Organic Polymer (COP) sensors (James et al., 2005). During the last two decades, however, a remarkable interest has been also focused on optical transduction principles for the measurement of chemical and biological quantities (Baldini et al., 2006). A large variety of devices based on optical methods have been used in chemical sensing and biosensing including ellipsometry, spectroscopy (luminescence, phosphorescence, fluorescence, Raman), interferometry (white light interferometry, modal interferometry in optical waveguide structures), spectroscopy of guided modes in optical waveguide structures (grating coupler, resonant mirror), and surface plasmon resonance (Wolfbeis, 2004; Zudans et al., 2004; Steinberg et al., 2003; Orellana, 2004; Homola et al., 1999; Mignani et al., 2005; Arregui et al., 2003; Brecht & Gauglitz, 1995; Gauglitz, 1996; Boisdé, 1996). In these sensors a desired quantity is determined by measuring refractive index, absorbance and fluorescence properties of analyte molecules or of a chemo-optical transducing medium. Optical fiber sensors are also very attractive in chemical sensing applications due to some unique characteristics deriving by the use of optical fibers, one of the most outstanding characteristic of which is their ability to transmit light over large distances with low losses allowing a sensor head to be remotely located from the instrumentation. This feature is particularly useful for sensing in harsh environments where hazardous chemicals may be present or extremes in temperature occur. In addition the small size, light weight and high flexibility of fibres allow access to areas that would be otherwise difficult to reach.

Provided the optical power density are within certain limits, fiber optic chemical sensors are much safer in explosive environments compared with sensors involving electrical signals, where a spark may trigger a gas explosion. Optical signals are immune to electrical or magnetic interference from, for examples, power lines and electrical machinery. Furthermore optical fibers have the capability of carrying a huge amount of information, much greater than that carried by electrical wires. Fiber optic sensing is very versatile, since the intensity, wavelength, phase and polarization of light can all be exploited as measurement parameters, and several wavelengths launched in the same fiber in either direction form independent signals. This gives the possibility to monitor several chemicals with the same fiber sensor or even simultaneously monitor unwanted environment

parameter variations which could drastically affect the chemical concentration measurements, such as the temperature or disturbance of the fiber. Multiplexing of fiber optic systems is also relatively easy, allowing expensive source or analysis instrumentation to be shared among a number of sites.

This contribution reviews the integration of carbon nanotubes as advanced sensitive coatings with optical fiber technology for the development of high performance opto-chemical sensors exploitable for several environmental monitoring applications. In particular, the excellent sensing capabilities of the realized photonic chemo-sensors against VOCs and other pollutants in air and water, at room temperature, will be reviewed.

2.1 Carbon nanotubes: advanced materials for chemical sensing

The search for new advanced materials is an important area of contemporary research in numerous disciplines of science. Great attention has been paid in recent years to nano-structured materials of different chemical composition, produced as nanoparticles, nanowires or nanotubes. Similarly, there has already been great interest in their preparation, properties and applications in the literature. As matter of fact, with the development of nano-science and nano-technology, a large number of literatures on one-dimensional nanostructured materials, including tubes, rods, belts, and wires in this area, have been published every year (Huang & Choi, 2007). These materials have their unique structures which are dominated by a wire-like structure whose diameter varies over a broad range from several tens of nanometers to a micrometer. In particular, carbon-based nanostructures exhibit unique properties and morphological flexibility, which renders them inherently multifunctional and compatible with organic and inorganic systems.

Carbon nanotubes (CNTs), discovered by Iijima in 1991 (Iijima, 1991) are at the forefront of the novel nanoscale investigations and nanostructure effects due to their unique electronic, chemical, structural, optical, mechanical and thermal properties depending on their specific hollow nanostructure with surface-arranged carbon atoms organized in rolled one-dimensional seamless tubes (Dresselhaus et al., 2001; Dai, 2002). They are considered as a new form of pure carbon, and can essentially be thought of as layers of graphite rolled-up into a tube to form a cylinder with diameter of few nanometers and length ranging from 1 to 100 microns. To date, CNTs are building blocks considered as the most promising functional nanomaterial for future miniaturized gas nanosensors due to their hollow nanostructure and high specific surface area which provide attractive characteristics for gas sensing applications. In fact, due to their unique morphology, CNTs possess the excellent capability to reversibly adsorb molecules of environmental pollutants undergoing a modulation of their electrical, geometrical and optical properties, such as conductivity, refractive index, thickness etc. CNTs can be distinguished in SWCNTs or multi-walled carbon nanotubes (MWCNTs) depending on whether only one layer or many layers of graphite are concentrically rolled up together, and can behave either as metallic or semiconducting, depending upon their diameter and chirality (the way the hexagons are arranged along the tubule axis) (Terrones, 2003). SWCNTs are a very important variety of carbon nanotube because they exhibit important electrical and sensing properties that are not shared by the MWCNTs variants. The purity of the CNTs affects their sensing performance, thus efficient purification protocols to remove metallic impurities and amorphous carbon particles have been developed as well (Penza et al., 2007_a).

2.2 Chemical sensors based on carbon nanotubes: state of the art

The special geometry of carbon nanotubes and their characteristic of being all surface reacting materials offer great potential applications as chemical sensor devices with excellent sensitivities and fast responses (Riu et al., 2008). Most of the sensors based on CNTs are field effect transistors (FET), since much interest has been focused in the past on the study of the changes in their electrical properties as a consequence of the interaction with gaseous and VOC molecules: many studies have shown that although carbon nanotubes are robust and inert structures, their electrical properties are extremely sensitive to the effects of charge transfer and chemical doping by various molecules. The electronic structures of target molecules near the semiconducting nanotubes cause measurable changes to the nanotubes electrical conductivity. Nanosensors based on changes in electrical conductance are highly sensitive, but they are also limited by factors such as their inability to identify analytes with low adsorption energies, poor diffusion kinetics and poor charge transfer with CNTs (Modi et al., 2003).

Kong et al. (Kong et al., 2000) were probably the first to show that CNTs can be used in chemical sensors since exposing SWCNTs to electron withdrawing (e.g. NO₂) or donating (e.g. NH₃) gaseous molecules dramatically increases or decreases the electrical resistance of SWCNTs in the transistor scheme. In addition CNTs-based sensors demonstrated a fast response and a higher sensitivity than, for example, solid-state sensors at room temperature. More or less in the same period, it was demonstrated that the electrical conductance of SWCNTs could be modified in presence of O₂ (Collins et al., 2000). The effect of the adsorption of several gas compounds in SWCNTs was also described (Sumanasekera et al., 2000), as well as those of water vapor on the electrical resistance of a SWCNT (Zahab et al., 2000). Shortly afterwards, Fujiwara et al. (Fujiwara et al., 2001) studied the N₂ and O₂ adsorption properties of SWCNT bundles and their structures. All these studies opened the door to the development of chemical sensors based on CNTs.

Sensing devices based not only on the changes in the electrical properties of CNTs but also on other principles were proposed. For example, bundles of SWCNTs (Adu et al., 2001) have measured the thermoelectric qualitative response to a variety of gases (He, N₂, H₂, O₂ and NH₃). Sumanasekera et al. (Sumanasekera et al., 2002) created a thermoelectric chemical sensor to measure the easily detectable and reversible thermoelectric power changes of SWCNTs when they are in contact with He, N₂ and H₂. Chopra et al. (Chopra et al., 2003) developed a circular disk resonator coated with SWCNTs using a conductive epoxy, which selectively detects the qualitative presence of several gases (NH₃, CO, Ar, N₂ and O₂) due to changes in the dielectric constant and shifts in the resonant frequency.

Wei et al. (Wei et al., 2003) demonstrated a gas sensor depositing CNT bundles onto a piezoelectric quartz crystal. This sensor detected CO, NO₂, H₂ and N₂ by detecting changes in oscillation frequency and was more effective at higher temperatures (200 °C). Penza et al. (Penza et al., 2004_a) developed SAW and QCM sensor coated with SWCNTs and MWCNTs and used them to detect VOCs such as ethanol, ethylacetate and toluene by measuring the downshift in the resonance frequency of the acoustic transducers.

Carbon nanotubes can be easily functionalized with molecules enabling the specific interaction with target chemicals thus improving the typically low selectivity of CNTs-based devices. In this way, different types of sensors based on molecular recognition interactions can be developed, allowing the development of nanosensors that are highly selective and sensitive. Chen et al. (Chen et al., 2003) used a non-covalent functionalized FET based on

SWCNTs for selectively recognizing target proteins in solution. Azanian et al. (Azanian et al., 2002) immobilized glucose oxidase on SWCNTs and enhanced the catalytic signal by more than one order of magnitude compared to that of an activated macro-carbon electrode. Zhao et al. (Zhao et al., 2002) worked with horseradish peroxidase and Sotiropoulou et al. (Sotiropoulou et al., 2003) worked with enzymes. Barone et al. (Barone et al., 2002) developed a device for β -D-glucose sensing in solution phase. They also showed two distinct mechanisms of signal transduction: fluorescence and charge transfer.

Recently, further interest has also been devoted to the possibility to change the optical and/or geometrical properties of SWCNTs upon adsorption of target analyte molecules, enabling to exploit such materials for the development of opto-chemical sensors for numerous environmental monitoring application, from chemical detection in air and water (Consales et al., 2006_a; Penza et al., 2004_b; Penza et al., 2005_b; Cusano et al., 2006_a; Consales et al., 2007_a) to hydrogen detection at cryogenic temperatures suitable for aerospace applications (Cusano et al., 2006_b). In particular, the possibility of exploiting such materials in conjunction with the optical fiber technology could enable the development of optoelectronic noses and tongues capable of air and water quality monitoring, characterized by ppm and sub-ppm resolutions, good recovery features and fast responses, as it will be seen in section 4 and 5.

3. Opto-chemical sensors in reflectometric configuration

The reflectometric configuration is essentially based on a low finesse and extrinsic Fabry-Perot (FP) interferometer and, as schematically shown in Fig. 1, uses a thin sensitive film deposited at the distal end of a properly cut and prepared SOF to produce a FP cavity. The first mirror is given by the fiber/sensitive layer interface whereas the second one is given by the sensitive layer/external medium interface.

Fig. 1. Schematic view of the Fabry-Perot-based configuration.

First described in 1899 by Fabry and Perot (Fabry & Perot, 1899), the interferometer known by their names makes use of multiple reflections between two closely spaced surfaces. In fact the light is partially reflected each time it reaches the second surface, resulting in multiple offset beams which can interfere with each other. The amount of light reflected at the first interface can be calculated as the sum of the multiple reflected beams and is strongly influenced even by very small changes of the distance between the two surfaces (the sensitive layer thickness) or its optical properties (the sensitive layer refractive index) (Dakin & Culshaw, 1988). This explains the massive use of such configuration in fiber optic-based sensing in the two past decades, especially for the detection and measurements of various physical, chemical and biomedical parameters (Jackson, 1994; Chan et al., 1994). All

these characteristics, combined with the possibility of integrating a number of sensitive materials with the optical fibers by means of very simple, low cost and versatile deposition techniques make it one of the most attractive and useful optoelectronic configuration especially suitable for practical applications.

The principle of operation of an optoelectronic sensor in reflectometric configuration relies thus on the fact that a modulation of the intensity of light reflected at the fiber-sensing overlay interface occurs due to changes in layer thickness (d_{film}) and complex refractive index ($\tilde{n}_{film}$). As matter of fact the fiber-film reflectance can be expressed as (Macleod, 2001):

$$R = \left| \frac{r_{12} + r_{23} \cdot e^{-i \cdot \tilde{k}_{film}}}{1 + r_{12} \cdot r_{23} \cdot e^{-i \cdot \tilde{k}_{film}}} \right|^2 \quad (1)$$

with:

$$r_{12} = \frac{n_f - \tilde{n}_{film}}{n_f + \tilde{n}_{film}}; \quad r_{23} = \frac{\tilde{n}_{film} - n_{ext}}{\tilde{n}_{film} + n_{ext}} \quad (2)$$

$$\tilde{k}_{film} = \frac{2\pi \cdot (2 \cdot \tilde{n}_{film} \cdot d_{film})}{\lambda} = \frac{4\pi \cdot n \cdot d_{film}}{\lambda} - i \frac{4\pi \cdot k \cdot d_{film}}{\lambda} = \beta_{film} - i\alpha \cdot d_{film}$$

where $\tilde{n}_{film} = n - i \cdot k$, $\alpha = 4\pi k / \lambda$ is the overlay absorption coefficient, n_f and n_{ext} are the optical fiber and external medium refractive index, and λ is the optical wavelength. Thus, the reflectance changes due to the chemical interaction between sensing overlay and target analyte can be expressed as follows:

$$\Delta R = \left(\frac{\partial R}{\partial n} \right) \cdot \Delta n + \left(\frac{\partial R}{\partial \alpha} \right) \cdot \Delta \alpha + \left(\frac{\partial R}{\partial d_{film}} \right) \cdot \Delta d_{film} = S_n \cdot \Delta n + S_\alpha \cdot \Delta \alpha + S_d \cdot \Delta d_{film} \quad (3)$$

where S_n , S_α and S_d are the sensitivities against the variations of the effective refractive index, the absorption coefficient and the overlay thickness, respectively. They strongly depend upon the geometrical and electro-optical properties of the sensitive nanocoatings and upon the environmental condition (for example vapor or liquid phase), and for this reason they have to be properly considered case by case. In particular, several effects could be involved to promote a reflectance change as a consequence of the analyte molecule adsorption within the sensitive overlay: first of all, swelling of the SWCNT nano-composite overlay that leads to a consequent increase of the film thickness; also, refractive index variations are expected due to the film density variation as expressed by the Lorentz-Lorentz law (Kingery et al., 1976). In addition, according to the plasma optic effect (Wooten, 1972; Soref & Bennet, 1987; Heinrich, 1990) a change either in the real part of the refractive index or in the absorption coefficient could be possible as a consequence of the free carrier concentration change induced by charge transfer mechanisms during analyte sorption. Modifications of film reflectance could be also possible due to optical absorption changes induced by chemical interaction with target analyte. In addition, it is noteworthy that, when very low chemical concentrations are considered (as in this work), it can be assumed that the analyte molecule adsorption occurs at constant overlay thickness ($\Delta d_{film} = 0$ in (3)).

3.1 Optoelectronic interrogation system

An important issue to address when dealing with sensors is the design and development of a proper demodulation unit able to provide a continuous interrogation of single or multiple sensor probes by minimizing size, complexity and increasing the cost effectiveness. So far, a variety of schemes have been proposed for the interrogation of a fiber optic sensor based on the FP cavity, the most used ones relying on spectrum-modulating approach and single wavelength reflectometry (Kersey & Dandridge, 2001). Here the attention has been focused on this last technique, which is simple to implement and requires just few widespread commercial and low-cost optoelectronic components while preserving excellent performance. In addition it enables the fabrication of cost-effective, reliable, robust and portable equipments, which are factors of crucial importance for in-situ and long-term monitoring applications and for the desired technology transfer to the market. The typical interrogation scheme enabling the reflectance monitoring of a FP cavity realized on the distal end of an optical fiber is shown in Fig. 2 (Consales et al., 2007_b).

It basically involves a superluminescent light emitting diode (with central wavelength $\lambda=1310$ nm and a bandwidth of approx. 40 nm), a 2x2 coupler and two photodetectors. It provides an output signal I that is proportional to the fiber-film interface reflectance R and that is insensitive to eventual fluctuations of the optical power levels along the whole measurement chain. As matter of fact, emitted light is splitted by the coupler and directed to the sensing probe (where partial reflection occurs) and to the first photoreceiver, whose output thus consists of an electrical signal (V_{source}) proportional to the power emitted by the source (P_{source}). Reflected light is directed through the coupler to the second photoreceiver which responds with an electrical signal (V_{signal}) proportional to P_{source} and to the overlay reflectance (R). The intensity compensation is obtained by considering the ratio between the voltage signals at the two photoreceivers:

$$I = \frac{V_{signal}}{V_{source}} = \alpha \cdot R \quad (4)$$

where α is a constant accounting for all the set-up parameters. In the followings, the relative change of the sensor output $\Delta I/I_0$ is considered (where I_0 is the output signal in the reference or initial condition), which, in turn, corresponds to the relative reflectance change occurring at the fiber-sensitive layer interface ($\Delta R/R_0$). Synchronous detection is typically implemented to enhance the system performance, by amplitude modulating the light source at 500 Hz and retrieving the photodetector voltages by using a dual channel lock-in amplifier. The minimum $\Delta R/R_0$ that can be detected by means of this interrogation system, calculated considering the maximum scattering on the sensor response in a steady-state level for a time interval of at least 10 minutes, is typically in the range $1-6 \cdot 10^{-4}$. In addition, a Time Division Multiplexing (TDM) approach is typically exploited to perform the quasi-simultaneous interrogation of up to eight optical probes by means of a fiber optic switch.

Fig. 2. Schematic illustration of the typical interrogation scheme adopted for the single wavelength reflectance monitoring of an optical cavity realized upon the fiber tip

3.2 Opto-chemical sensor fabrication

The realization of thin films of SWCNTs with a controllable thickness is an important basis for the future development of their scientific understanding and technological applications. Proper manipulation techniques are required for applying thin-films of carbon nanotubes on substrates that do not allow direct grow methods. Although various proposals exist for their incorporation into devices, in single tube or thin film architectures (Bachtold et al., 2001), here the Langmuir Blodgett (LB) technique has been chosen as way to transfer nanometer-scale layers of SWCNTs upon either bare optical fibers or Cadmium Arachidate (CdA) buffer-linker material, previously deposited (by the same technique) upon the fiber end in order to improve the carbon nanotubes adhesion on the sensors surface. The CdA has been chosen as buffer material due to its peculiar amphiphilic molecular structure suitable for LB deposition process (Takamoto et al., 2001; Di Luccio et al., 2004).

The LB-technique is one of the most promising techniques for preparing such thin films as it enables the precise control of the monolayer thickness, homogeneous deposition of the monolayer over large areas and the possibility of making multilayer structures with varying layer composition (Roberts, 1990). An additional advantage of the LB technique is that monolayers can be transferred on almost any kind of solid substrate. However these advantages have to be traded with the low speed of the deposition procedure as well as the limited number of materials suitable for this technique. As represented in Fig. 3, the molecules of the films to deposit are firstly dispersed onto the surface of a sub-phase, typically oriented with the hydrophobic part upwards and with the hydrophilic one immersed in water. Subsequently, a reduction of the surface area occupied by each molecule is performed by means of moving barriers in order to produce a solid phase of a given surface pressure in which the molecules are densely packed forming an highly ordered array (James & Tatam, 2006). From this phase the molecules can be transferred to a properly cleaned and prepared solid substrate by its dipping through the condensed Langmuir layer. As the solid phase is reached only at high surface pressures, a continuous reduction of the moving barriers is performed when the molecules are transferred from the sub-phase to the substrate in order to keep the surface pressure constant, ensuring that the solid phase is maintained. Repeated dipping of the same substrate are also possible, resulting in the deposition of a thin film one monolayer at a time.

Fig. 3. Schematic representation of the Langmuir-Blodgett deposition procedure.

For CdA buffer multilayer deposition, a solution (0.953 mg/ml) of arachidic acid [$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$] in chloroform is typically spread onto a sub-phase of deionized water (18 M Ω) containing 10^{-4} M cadmium chloride (CdCl_2). The sub-phase pH is kept constant at a value of 6.0, with the temperature fixed at 23°C. The monolayer is compressed with a barrier rate of 15 mm/min up to a surface pressure of 27 mN/m. The single layers is deposited on the SOF with a vertical dipping rate of 12 mm/min. After a proper drying of 24 hours, the coated fiber is ready for the deposition of the CNT sensing layers.

For SWCNT film deposition, a solution (0.2 mg/ml) of SWCNT pristine material in chloroform is spread onto a sub-phase constituted by deionized water (18 M Ω) with 10^{-4} M of CdCl_2 . The sub-phase pH and the temperature are kept constant at values of 6.0 and 23°C, respectively. The monolayer is compressed with a barrier rate of 15 mm/min up to a surface pressure of 45 mN/m. The single layer is deposited on the SOF surface, either bare or already coated by 20 monolayers of CdA (Penza et al., 2005_b), with a dipping rate of 3 mm/min. After a proper drying of 12 hours overnight, the sensing multilayers deposited are ready for the experimental testing. The raw pristine material of commercial SWCNTs has always been used as-bought, without any purification treatment. The samples are prepared by sonicating SWCNT suspension in chloroform for 1 hour at room temperature prior to the deposition. It is also noteworthy that before the LB deposition procedure the SOFs are previously accurately polished from the acrylic protection and cleaved with a precision cleaver in order to obtain a smooth and plane surface. Then, they are washed in chloroform and dried with gaseous nitrogen to be ready for the deposition. The number of deposited CdA and/or SWCNT monolayers are controlled by choosing how many times the substrate is dipped inside or lifted from the solution containing the monolayer to transfer.

3.3 Structural and morphological characterization of SWCNT overlays

The rational design of a chemical sensor and of its performance is something which is possible only if the sensitive material properties and the way they are affected by different deposition parameters or ambient conditions are well known and understood. To this aim an extensive characterization of the as-bought SWCNT powders as well as of the deposited LB SWCNT films has been carried out in order to investigate their structural and

morphological features. Such characterization involved X-ray diffraction (XRD) and Raman Spectroscopy analyses, High-Resolution Transmission Electron Microscopy (HRTEM) and Scanning Electron Microscopy (SEM) observations. In particular, in Fig. 4.a is reported the typical XRD spectrum of as-bought SWCNT powder (1 mg) material. The pattern exhibits a well-defined graphite-like (002) diffraction peak at $2\theta = 26.5^\circ$, and a broad band centered at lower $2\theta = 22^\circ$ from amorphous carbon or non-nanotube carbon material.

Further XRD analyses performed on CdA multilayers on glass substrates evidenced a CdA monolayer spacing of about 2.8 nm for cadmium arachidate. The same measurements, performed with a SWCNT multilayer, revealed a carbon nanotubes monolayer spacing of about 2.0 nm (Penza et al., 2005_b). Also Raman spectroscopy analyses have been conducted to characterize the fabricated LB films based on SWCNTs already deposited on the SOF tip. To this aim, a Raman microscope functioning in backscattering configuration employing a HeNe laser (633 nm) and 50x and 100x objective lenses was used. The results are shown in Fig. 4.b, where the typical Raman spectrum of a SWCNT film is reported. The characteristic multi-peak feature “G-band” at about 1580 cm^{-1} , corresponding to carbon atoms vibration tangentially with respect to the nanotube walls (Saito et al., 1998), together with the less remarkable disorder-induced “D-band” peak typically in the range $1300\text{--}1400\text{ cm}^{-1}$, representing the degree of defects or dangling bonds, can be easily revealed.

Fig. 4. (a) X-ray diffraction spectrum obtained from HiPco SWCNT powder (1 mg) and (b) typical Raman spectrum of a LB SWCNT film directly deposited on the optical fiber tip.

In particular the observation of the two most intense G peaks (labelled G^+ and G^-) confirm the single-walled nature of the carbon tubes while their predominant semiconducting behavior can be derived by the Lorentzian lineshape of the G^- feature which, on the contrary, is broadened for metallic SWCNTs (Saito et al., 1998). In addition, the large ratio of G to D peaks give us an indication of an ordered structure of the deposited SWCNT overlay. It is worth noting that, since the Raman studies have been performed on SWCNT film already deposited on the fiber end-face, the results shown also confirm their successful integration with optical fiber technology. The HRTEM images of a SWCNT powder, reported in Fig. 5 at (a) low and (b) high magnification, confirm the nanometric dimension of the carbon tubes and reveal the presence between them of some Fe metal particles, a typical catalyst used in the HiPco production process of carbon nanotubes.

Finally, in Fig. 5.c is reported the typical SEM images of CdA-buffered LB SWCNT films deposited upon a SOF tip. It demonstrates once more the success of the integration of carbon nanotubes with the optical fiber and reveals their attitude to adhere one to each other forming bundles or ropes with a spaghetti-like arrangement.

Fig. 5. HRTEM images of SWCNT powder at (a) low and (b) high magnification and (c) SEM images of CdA-buffered SWCNT LB films deposited on a SOF tip.

4. Environmental monitoring applications: Experimental Results

In the following we report the results obtained during the last years of research focused on the development of SWCNTs-based fiber optic chemo-sensors. In particular, we focus our attention on chemical trace detection in air and water, at room temperature. The strong potentiality of this novel SWCNTs-based fiber optic sensing technology to be employed for numerous practical environmental monitoring application is clearly demonstrated.

4.1 Room temperature detection of VOCs in air

The investigation and characterization of the VOC detection performance of SWCNTs-coated opto-chemical sensors has been carried out by means of an experimental setup ad hoc designed and realized, a schematic representation of which is reported in Fig. 6.

Fig. 6. Experimental setup used for the vapor testing.

In particular the optical fiber probes are located in a properly designed test chamber realized in stainless steel. The volume of the test chamber was 1200 ml, the total flow rate per exposure has been kept constant at 1000 ml/min and the vapors have been generated by the bubbling method. The gas flow rate has been controlled by a mass flow-meter driven by a controller-unit communicating with a PC via standard RS-485 serial bus. The controller unit was able to drive up to eight different gas-channels, and the gas flow rate in each gas-channel was regulated by a dedicated mass flow meter with a full scale of the mass flow ranging from 10 to 1000 ml/min. Numerous tests have been performed by using nitrogen or dry air as reference and carrier gas to transport the generated vapors inside the test ambient: dry air has been chosen because of the higher stability demonstrated by the optical fiber sensor signals. All the experiments have been conducted at room temperature.

The capability of SWCNT overlays of undergoing changes in their complex refractive index and thickness as consequence of the adsorption of target analyte molecules was demonstrated for the first time in 2004 (Penza et al., 2004). In that case LB films consisting of SWCNT bundles were transferred upon the optical fiber tip by using a buffer LB multilayer of CdA pre-deposited on the sensor surface in order to promote the CNT adhesion. The fabricated probes were exploited for the detection of several VOCs, such as isopropanol, methanol, ethanol, toluene and xylene. However, in 2005, multilayers of SWCNTs with different thicknesses were successfully deposited directly upon the optical fiber surface by a modification of the LB process (Consales et al., 2006_b), resulting in an improvement of the sensing performance of the un-buffered configuration with respect to the buffered case, especially in term of sensor sensitivity. As an example, Fig. 7 shows the highest $\Delta R/R_0$ exhibited by a fiber optic probe coated with 4 SWCNT monolayers (namely SOF-4) when exposed to 30-minutes decreasing concentration pulses of xylene vapors with respect to the counterpart optoelectronic sensor arranged in the CdA buffered configuration (2 monolayers of SWCNTs deposited onto 20 monolayers of CdA). In both cases, significant reflectance changes occurred on analyte exposure as consequence of the variation in the SWCNT overlay refractive index promoted by toluene molecules adsorption.

Fig. 7. $\Delta R/R_0$ occurred on xylene vapor exposure to CdA-buffered and un-buffered SWCNTs-based opto-chemical sensors, at room temperature.

Both sensors exhibited the capability of detecting the chemical under investigation at ppm traces combined with fast response, complete reversibility (enabling the reuse of the sensor after a given measurement) and a marked response time dependence on analyte concentration. However the sensor SOF-4 provided response changes more than one order of magnitude higher than the ones provided by the counterpart probe in the CdA-buffered configuration. In light of this results, strong interest was devoted to the investigation of the sensing capabilities of SWCNTs-based opto-chemical sensors arranged in the un-buffered configuration against several VOCs.

In Fig. 8.a are reported the results of toluene vapor testing carried out by exposing the probe SOF-4 to four toluene pulses with concentration in the range 54-93 ppm. The results obtained confirmed the behavior of the fiber optic sensor exhibited during xylene testing: as matter of fact, also in this case a $\Delta R/R_0$ increase on exposure was observed as consequence of analyte molecule adsorption. A less pronounced dependence of the response time on toluene concentration was noticed, revealing that different adsorption dynamics occur depending on the VOC under investigation. Also, a slight drift in the signal baseline can be recognized, due to little thermal changes in the not perfectly thermo-stated test chamber.

In order to investigate the reliability of the proposed transducers, a repeatability test has been carried out for the same fiber optic sensor. The results are shown in Fig. 8.b, where the $\Delta R/R_0$ occurred as consequence of two xylene exposures at 21 ppm are reported. As evident, the opto-chemical probe demonstrated high repeatability and reliability also at very low analyte concentrations.

Fig. 8. (a) Response of sensor SOF-4 to toluene vapors at room temperature and (b) repeatability test performed exposing the same sensor to 2 pulses of xylene vapors (21 ppm).

These results have to be considered at constant temperature, because no thermal variation occurred meanwhile. However it is evident that monitoring of thermal drifts and compensation of their effects on sensor response are strictly required to not affect the system performance. Temperature monitoring could be implemented by means of proper fiber bragg grating temperature sensors, which could be either separately inserted within the test ambient or integrated with the optical fiber probe (Cusano et al., 2004). Similarly, CNTs-based fiber optic chemo-sensors demonstrated a relevant sensitivity also to humidity changes (Consales et al., 2006_b), thus revealing the necessity of proper calibrations and compensations of the sensor response, especially when high accuracy is requested.

In Fig. 9 have been reported the calibration curves of sensor SOF-4 obtained against toluene and xylene vapors, which revealed an almost linear behavior in the investigated concentration ranges. In addition, by comparing sensor sensitivities to both analytes, calculated as relative reflectance change upon concentration unit ($S_{analyte}=(\Delta R/R_0)/C$) (D'Amico & Di Natale, 2001) a SOF sensitivity to xylene ($S_{xylene}=1.1 \cdot 10^{-3} \text{ ppm}^{-1}$) more than two times higher than that to toluene ($S_{toluene}=4.7 \cdot 10^{-4} \text{ ppm}^{-1}$) has been found. Considering the minimum $\Delta R/R_0$ achievable with the exploited interrogation unit, a resolution of approx. 290 ppb and 120 ppb have been estimated for toluene and xylene, respectively.

Fig. 9. Calibration curves of sensor SOF-4, exposed to toluene and xylene vapors.

This excellent resolutions are more than three orders of magnitude higher than that obtained by means of a fluorosiloxane polymer-based Surface Plasmon Resonance (SPR) optical fiber sensor (900 ppm and 190 ppm, respectively for toluene and xylene) (Abdelghani & Jaffrezic-Renault, 2001), and more than two orders of magnitude higher than that provided by a multimodal optical fiber sensor sensitized by phenyl-modified porous silica (100 ppm and 20 ppm, respectively) (Abdelmalek et al., 1999).

4.1.1 Influence of monolayers number and CdA buffer on sensor sensitivity

Here, the influence of the number of SWCNT monolayers on the sensor performance are discussed. The differences between the sensing capability of buffered and un-buffered configurations are also better discussed. To this aim, four opto-chemical sensors coated by different numbers of monolayers, directly deposited on bare substrates and also buffered by 20 LB monolayers of CdA, have been simultaneously exposed to toluene and xylene vapors. Fig. 10.a reports the $\Delta R/R_0$ versus toluene concentration for all the tested sensors. It can be seen that a sensitivity increase has been obtained by passing from 2 ($0.9 \cdot 10^{-4} \text{ ppm}^{-1}$) to 4 SWCNT monolayers ($4.7 \cdot 10^{-4} \text{ ppm}^{-1}$). On the contrary, the optical chemo-sensor coated by a higher number of monolayers (12), and thus by a thicker SWCNT film, exhibited a negative sensitivity ($-0.7 \cdot 10^{-4} \text{ ppm}^{-1}$). This means that for this sensor the fiber-film interface reflectance decreases on exposure. This is due to the fact that the film reflectance, and thus also the sensor sensitivity, is strongly dependent on the thickness and refractive index of the CNT overlay, in accordance with (1). As a matter of the fact, depending on the geometric features of the film deposited atop the optical fiber, either positive or negative sensitivities to a target analyte can be obtained.

Fig. 10. Calibration curves and sensitivities obtained by exposing four fiber optic sensors coated by a different number of SWCNT monolayers to (a) toluene and (b) xylene vapors.

For the same reason, the CdA buffer multilayer, whose optical properties are quite similar to those of the standard optical fibers, and thus not optimized for the particular configuration exploited, dramatically decreases the sensitivity of optical fiber sensors ($-0.4 \cdot 10^{-4} \text{ ppm}^{-1}$). It is noteworthy, however, that by choosing a buffer-linker material whose optical and geometrical features (such as the multilayer thickness and refractive index) are well optimized for the specific configuration, one could be able to strongly enhance the SOF sensor performance. From Fig. 10.b it can be seen that the four fiber optic chemo-sensors exhibited the same behaviors also in case of xylene vapor testing: hence, it demonstrates that the inversion of the optoelectronic sensor sensitivities is not due to the particular analyte tested, but to the optical configuration exploited. This feature could be very useful for pattern recognition analysis in case of multi-transducer approaches, where complementary sensors are exploited to improve the analyte discrimination (Penza et al., 2005_b).

4.1.2 Response and recovery time analysis

As the experimental results revealed a dependence of sensor response times (and as consequence of the adsorption/desorption dynamics) on analyte concentration, a detailed analysis of response and recovery times of sensor SOF-4 has been performed (Consales et al., 2007_b) by its exposure to different concentration pulses of toluene and xylene vapors (the exposure time was 30 minutes). The response (recovery) time has been calculated as the time the output signal needed to pass from 10% to 90% (from 90% to 10%) of the total signal variation. The results obtained for both chemicals are quite similar and revealed the attitude

of response time to increases with analyte concentration while the recovery time is quite constant. In particular, the minimum response time in case of toluene, obtained for 54 ppm, was approx. 7 minutes while the maximum one, obtained for 93 ppm, was approx. 11 minutes. The recovery time was as low as approx. 5 minutes. Slower responses were observed in case of xylene exposure, for which the SOF response times increased from approx. 4 minutes (3 ppm) to approx. 18 minutes (39 ppm), and the recovery time was approx. 6 minutes. This could be ascribed to a different adsorption kinetic of the two analyte molecules inside the CNT sensitive nanocoatings. It is noteworthy, however, that the response times of the proposed fiber optic chemo-sensors are relatively good taking into account the volume of the test chamber and the total flow rate per exposure. It is also important noting that although these times could be reduced by depositing a lower amount of carbon nanotubes on the SOF tip, the choice of the geometric features of the sensitive overlay has to be made by considering the trade-off that exists between sensor sensitivity and response (and recovery) time (Consales et al., 2007_b).

4.2 Towards fiber optic tongue: chemical trace detection in water

In this section the attention has been focused on the feasibility of exploiting the excellent sensing properties of CNTs for the development of high performance optoelectronic sensors capable of chemical trace detection in aqueous environments, at room temperature.

A schematic view of the experimental setup exploited for chemical trace detection in water is reported in Fig. 11.a. The SWCNTs-based opto-chemical transducers have been inserted in a beaker containing pure water. The presence within the test ambient of the analyte under investigation has been promoted by its injection inside the beaker. The injected volume has been chosen, each time, in order to obtain the desired analyte concentration. The polluted water has been continuously stirred to ensure maximum dispersion of analyte. In addition, after each exposure, the capabilities of SOF sensors to recover the initial steady state level have been investigated by restoring the initial condition of pure water: pure water has been continuously injected in the test chamber, while the contaminated water, previously present in it, contemporarily stilled out.

Fig. 11. (a) Experimental setup exploited for chemical trace detection in water and (b) $\Delta R/R_0$ occurred to the sensor SOF-12 on toluene injections, at room temperature.

The results obtained exposing a SOF sensor coated by 12 monolayers of SWCNTs (SOF-12) to several injections of toluene in water, with concentrations in the range 20-80ppm (calculated as $\mu\text{l/l}$), are shown in Fig. 11.b. They revealed a sensitivity in air higher (approx. $1.5 \cdot 10^{-4} \text{ ppm}^{-1}$) than that obtained in case of water environment (approx. $1.2 \cdot 10^{-4} \text{ ppm}^{-1}$). The differences can be ascribed to the dependence of the reflectance upon the surrounding refractive index combined to different adsorption characteristics occurring in liquid environment, especially if the kinetic is diffusion limited.

Fig. 12. (a) Calibration curves of sensor SOF-12 against toluene in air and aqueous environments and (b) characteristic times of the same sensor on toluene exposure in water.

Taking into account the sensitivity of the sensor against toluene and considering the $\Delta R/R_{0min}$ ($6 \cdot 10^{-4}$) obtainable with the exploited instrumentation, a resolution of 5 ppm has been estimated. Finally, an analysis of the response (t_{10-90}) and recovery (t_{10-90}) times of the optical probes has been carried out. The results obtained for the detection in water are shown in Fig. 12.b and reveal characteristic times slightly dependent on analyte concentration, with the mean response time (approx. 20 min.) higher than the mean recovery one (approx. 4 min.). A clear difference has been found with respect to the characteristic times obtained in case of in air detection, where the same sensor exhibited mean response and recovery times (towards toluene) of approx. 8 and 28 min., respectively.

4.3 Discussion

Here, a brief discussion concerning some of the typical drawbacks arising from the use of carbon nanotubes as sensitive elements of reflectometric optical fiber sensors is carried out, which evidences some currently unsolved matters, but, at the same time, opens the way to further investigations and research activities. First of all, the attitude of SWCNTs to randomly distribute in tangled networks of nanotubular chains and densely aggregate mats causes a not very high repeatability of the distribution of carbon nanotubes upon the sensor surface as well as their optical properties. These drawbacks could be overcome by means of an alignment of the carbon nanotubes onto the sensor substrate, which should provide a better and almost predictable SWCNT distribution upon them (Yoo et al., 2005).

The adhesion of the carbon nanotubes to the fiber substrate also requires further investigations and improvements, especially when the SWCNTs-based sensors are exploited for in water chemical detection applications, for which particularly hard operating conditions could even promote a detachment of the sensitive overlay from the optical fiber

tip. A first attempt to improve the adhesion of SWCNT overlays to the distal end of the optical fibers is reported in the next section and relies on their embedding in CdA host-matrix in order to obtain nanocomposites with tailored amount of nanotube filler contents. Finally, another issue to address is related to the poor selectivity of the proposed SWCNTs-based sensors towards a given chemical specie. This means that in case of a multicomponent gas mixture with interfering analytes, the information provided by the sensors could be ambiguous and no straightforward information about the test environment could be achieved. This is a very common aspect in chemical sensing applications as demonstrated by the strong effort which is currently devoted by the researchers on how to improve the sensor discrimination ability among different analytes. Basically, there are two possible approaches in the attempt to increase the chemical sensor selectivity, and both have to be followed in synergy. The first one is a direct approach which relies on the sensitive layer functionalization in order to have an higher affinity of the material towards specific chemical species (Balasubramanian & Burghard, 2005). The second one is based on the use of a hybrid system composed of multiple transducers coated by the same material (or, in the most general case, by different materials) in the form of an array. Here, sensors with a poor selective response, when considered collectively, provide unique patterns typical for each analyte. The generated response patterns are interpreted by pattern-recognition algorithm for the selective detection (Zarcomb & Stretter, 1984). Section 5 is focused on this last approach: in particular it will be shown that the use of standard pattern recognition techniques, such as the Principal Component Analysis (PCA), applied on both the static and dynamic responses of the single sensor of a fiber optic sensor array enables to significantly enhance the discrimination ability of the SWCNTs-based optoelectronic sensors.

5. SWCNTs-based nanocomposites as advanced nano-coatings

As already discussed in section 4.3, the adhesion of carbon nanotubes to the fiber substrate and the poor repeatability of the deposition process (especially concerning the distribution of the tubes upon the fiber tip as well as the optical properties of the fabricated layer) represent two important issues to improve for an extensive exploitation of the proposed SWCNTs-based opto-chemical sensors for practical applications and for their effective transfer to the market. The alignment of carbon nanotubes upon the sensor substrate as well as the embedding of controlled quantity of them inside a host-matrix of a foreign material for the synthesis of nanocomposites with tailored amount of nanotube filler contents have been identified as possible ways to overcome these drawbacks. In fact, the CdA was used in the past as buffer-linker material to promote the adhesion of SWCNT thin films to the fiber end-face. Here the attention has been focused on the latter solution. In particular, the sensing performance of fiber optic chemo-sensors based on nanocomposite overlays of SWCNTs embedded in a CdA matrix have been investigated against several chemicals both in gaseous (hydrocarbons, alcohols and NO₂) and liquid phase (toluene and xylene), at room temperature.

5.1 CdA/SWCNTs-based sensors fabrication and characterization

The Langmuir-Blodgett deposition process has been exploited again as a way to transfer thin films of SWCNTs-based nanocomposites upon the distal end of properly prepared single-mode optical fibers. The CdA has been chosen as host-matrix material to incorporate

the SWCNTs in the nanocomposite due to its peculiar amphiphilic molecular structure suitable for LB deposition process and because of the know-how already experienced by the authors in the integration of such material and the optical fiber transducers (Penza et al., 2005_b; Cusano et al., 2006_b). Two separate solutions of arachidic acid in chloroform and SWCNTs in chloroform have been mixed in order to prepare a final solution of chloroform with arachidic acid (0.25 mg/ml) and SWCNTs (0.19 mg/ml). The concentrations and the volumes of the initial solutions were chosen to obtain a weight percentage of the filler component (SWCNTs) with respect to the matrix-component (CdA) of approximately 75 wt. %. However, different concentrations of arachidic acid and SWCNTs in the final solution could also be exploited for the preparation of composites with different weight percentages. The mixed solution was then accurately dispersed and stirred in an ultrasonic bath for 1 h. Subsequently, 160 μ l of the mixed solution were spread onto a sub-phase constituted by acetate buffer with CdCl_2 10^{-4} M. The pH and the temperature of the sub-phase were kept constant at 6.0 and 20° C, respectively. The monolayer of the nanocomposite was compressed with a barrier rate of 15 mm/min up to a surface pressure of 27 mN/m. The single composite monolayer was deposited upon the fiber surface with a dipping rate of 14 mm/min. The optical fibers used for the deposition have been previously accurately polished from the acrylic protection and cleaved with a precision cleaver. Then, they have been washed in chloroform remove any residual coating. Repeated dipping of the fiber substrates through the condensed Langmuir layer have been performed, resulting in the deposition of multilayered CdA/SWCNT films one monolayer at a time. Fig. 13 shows the typical SEM photograms, at (a) low and (b) high magnification, of a multilayer constituted by 20 monolayers of CdA/SWCNT nanocomposite at 27 wt. % (deposited upon a glass substrate). The typical bundle disposition of the carbon nanotubes together with their good cadmium arachidate-assisted adhesion to the surface can be easily observed. A detailed morphological and structural characterization of the carbon nanotubes-based composites deposited by the LB method has been carried out by Penza et al. (Penza et al., 2006_b). Instead, here, the results of Raman spectroscopy analysis are reported, conducted with the aim of characterizing the fabricated nanolayers of CdA/SWCNTs (already deposited on the optical fiber tip) and compare them with the standard SWCNTs one. To achieve this purpose, a Raman microscope functioning in backscattering configuration employing a HeNe laser (633 nm) and 50x and 100x objective lenses was used.

Fig. 13. SEM image of a CdA/SWCNT overlay with a filler content percentage of 27 wt. %, at (a) high and (b) low magnification, deposited upon a glass substrate; (c) Raman spectra of SWCNT and CdA/SWCNT LB overlays directly deposited on the optical fiber end-face.

The results are shown in Fig. 13.c, where the typical Raman spectra of SWCNTs and CNT-based composite layers, already deposited upon the fiber end-face, have been reported. No significant differences between the two recorded spectra can be observed, thus evidencing that no degradation of the CNT occurred due to their inclusion within the CdA matrix.

5.2 VOC detection in air at room temperature

The room temperature sensing performance of the fabricated probes have been investigated both in air and water environments and have been compared with those obtained with the same transducers coated by un-buffered SWCNT overlays. Here the attention is focused on trace detection of four VOCs (toluene, xylene, ethanol and isopropanol) and one gas (NO_2) by using a sample coated by 10 monolayers of nanotubes-based composite with a SWCNT filler weight percentage of approximately 25 wt.%. The results are shown in Fig. 14, where, in particular, the $\Delta R/R_0$ occurred on exposure to toluene and ethanol vapors have been reported. The analyte adsorption within the SWCNTs-based nanocomposite overlay was able to induce a significant increase of the fiber-film reflectance as consequence of the complex refractive index change in the FP sensing cavity. The experimental data clearly reveal the capability to detect very low concentrations of the tested pollutants at ppm levels, as well as its quite good attitude to recover the initial baseline signal upon the complete analyte molecule desorption. This feature is of great importance for chemical sensing since it enables the sensor to be easily and quickly reused after a given measurement, avoiding ad hoc cleaning procedures, that are costly and time-consuming. In particular, the sensor exhibited a complete and fast reversibility of the response in case of toluene exposure, however this is not the case of ethanol test for which the reference signal corresponding to the condition of uncontaminated ambient is not fully recovered. This behavior was also observed on isopropanol exposure and could be attributed to the higher polarity of this kind of chemical species (alcohols). Different xylene and ethanol sensitivities have been measured for the CdA/SWCNTs-based fiber probe (approx. $1.3 \cdot 10^{-3} \text{ ppm}^{-1}$ and approx. $5 \cdot 10^{-4} \text{ ppm}^{-1}$, respectively). In addition, the different response dynamic can be attributed mainly to the different diffusivities of toluene and ethanol molecules within the nanocomposite overlay.

Fig. 14. Time response of the photonic sensor coated by 10 monolayers of CdA/SWCNT nanocomposite (25 wt. %) to (a) toluene and (b) ethanol vapors, at room temperature.

Fig. 15.a reports the response of the same CdA/SWCNTs-based sensor to five NO_2 pulses with concentrations in the range 1-10 ppm. Also in this case the sensor turned out to be capable of detecting very small traces of the gas under test and, similarly to what observed for alcohol detection, a baseline shift occurred upon multiple exposures of NO_2 . However, in this case the drift is thought to be mainly caused by the fact that the time extent between two successive NO_2 exposures is not sufficiently high to let the sensor to completely recover its initial baseline. This is demonstrated by the fact that after the last exposure the baseline value is similar to the one recorded before the first exposure. Combined with this effect, a slight drift of the baseline intensity is also present, that could be attributed to a strongest interaction between NO_2 and CdA/SWCNT overlay. Also a chemical modification of the overlay could be possible. In both cases, a modification of the nanocomposite refractive index is expected. The same can be said for the case of ethanol adsorption. It is also worth noting that for NO_2 detection the fiber optic transducer exhibited a $\Delta R/R_0$ of opposite sign with respect to that observed in case of vapor detection. This interesting behavior has been observed also for the fiber optic sensors in the standard configuration (i.e. fiber optic coated by pure SWCNTs), and could be ascribed to the electrical nature of the analyte under investigation, electron donor (vapors) or acceptor (NO_2). In particular it could be due to the influence that the charge transfer induced by the analyte molecule adsorption within the sensitive material has on the optical properties of SWCNTs-based overlay itself. In light of this consideration, the plasma optic effect (Wooten, 1972; Soref & Bennet, 1987; Heinrich, 1990) is also being considered, that allows one to relate the modulation of the optical properties of sensitive overlays (refractive index and absorption coefficient) to the changes in its free carrier concentration. In order to better clarify this aspect, further measurements are currently in progress involving more analytes with varying charge transfer properties as well as transducers with different principles of operation (mainly resistive, capacitive and mass-sensitive) coated by the same SWCNTs-based materials. However, to support our conjecture, preliminary experiments have been conducted with the aim of measuring the electrical response of a SWCNTs-based composite layer upon NO_2 exposure.

Fig. 15. (a) $\Delta R/R_0$ of the opto-chemical sensor coated by 10 nanocomposite monolayers (25 wt. %) and (b) electrical resistance versus time of a CdA/SWCNT thin film on exposure to different concentrations of gaseous NO_2 , at room temperature.

To this aim, a direct measure of the d.c. electrical conductance of the composite films deposited onto rough alumina (5.0 mm length x 5.0 mm width x 0.5 mm thickness) substrates with 200 μm pitch interdigitated Cr/Au (20 nm/200 nm thick) pattern by means of two-pole probe method with an electrometer (Keithley 617) has been carried out.

Fig. 15.b reports the typical time response of the electrical resistance of a LB layer of CdA/SWCNTs composite upon exposure of NO_2 , at room temperature. As expected, it decreases when the composite film is exposed to the oxidizing NO_2 gas. In particular, electron charge transfer occurs from SWCNTs-based composite to NO_2 because of the electron-accepting power of the NO_2 molecules. Thus, the NO_2 gas depletes electrons from the SWCNTs-based composite, increases the concentration of electrical holes in the p-type SWCNTs-based composite, hence causing the electrical resistance to decrease. Even if a partial desorption and an un-reached saturation level can be observed, similarly to the case of optical sensors, however a clear electrical response modulated by the gas adsorption is demonstrated, revealing that a charge transfer effectively occurs between the realized LB SWCNT overlays and the analyte under investigation.

Furthermore, an almost linear behavior in the sensor calibration curves (reported in Fig. 16) has been found towards most of the tested chemicals in the investigated ranges, as well as a higher sensitivities (see Fig. 17.a) in case of exposure to aromatic hydrocarbons ($3.2 \cdot 10^{-3} \text{ ppm}^{-1}$ and $1.3 \cdot 10^{-3} \text{ ppm}^{-1}$ respectively for xylene and toluene) than to alcohols ($5 \cdot 10^{-4} \text{ ppm}^{-1}$ and $4 \cdot 10^{-4} \text{ ppm}^{-1}$ respectively for isopropanol and ethanol). In addition the sensitivity towards NO_2 was of approx. $-1.3 \cdot 10^{-3} \text{ ppm}^{-1}$. By considering the minimum detectable $\Delta R/R_0$ achievable with the exploited interrogation system, resolutions (calculated as $\Delta R/R_{0\text{min}}/C$, where C is the analyte concentration) in the range 30-80 ppb and 200-250 ppb have been estimated respectively for hydrocarbon and alcohol detection, while the minimum concentration of NO_2 that can be detected turned out to be approx. 80 ppb.

Fig. 16. Sensor characteristic curves obtained for the five tested chemicals.

Moreover, the analysis of the mean response time revealed that the CdA/SWCNT composite-based sensor provides a faster response (see Fig. 17.b) in case of alcohol exposure (8 and 9 minutes, respectively) than in the hydrocarbon one (33 and 31 minutes, respectively). In particular, the ratio between the mean response time in case of toluene and ethanol detection is approx. 3.4, while the one obtained with standard SWCNTs is approx. 15. This means that the presence of the CdA matrix not only slows the sensor response down but also leads to significant differences in the adsorption dynamics of the two

analytes. In addition, since the diffusivity depends upon the exploited SWCNT filler content, it is expected that variations in the SWCNT weight percentage within the CdA matrix could be able promote differences in the sensor response times. In order to investigate this aspect, further experimental measurements will be performed, involving sensors with different wt. percentages of CNTs.

The opto-chemical sensors based on CdA/SWCNTs exhibited quite high response times; this could be mainly due to the fact that the molecules of the target analyte adsorb not only at the side-wall of the carbon nanotubes, but also in the interstitial sites between the tubes (Fujiwara et al., 2001). In particular, in case of film consisting of bundles of SWCNTs, the latter contribution could significantly slow down the sensor response times (Kong et al., 2000). However it is worth noting that these times are comparable with those obtained by means of many sensors based on different transducing principles (conductometric, resonator, mass-sensitive sensors, etc.) but integrating the same sensitive materials (Kong et al., 2000, Chopra et al., 2003, Penza et al., 2005_b, Lucci et al., 2005). Also, it can be attributed to the presence of the CdA matrix and thus to the diffusion rates of analyte molecules inside the CNT composite. It is also important noting that the content of SWCNTs within it can also influence the diffusion times and the sensor sensitivity (as already reported for the electrical case with CdA/SWCNTs-based SAW sensors (Penza et al., 2006_b; Penza et al., 2007_b). These aspects, however, are still under investigation. The bar plots reported in Fig. 17 can be used also to compare the sensing performance of the nanocomposite-based probe with the results obtained with that coated by 10 monolayers of SWCNTs directly deposited atop the fiber end: the use of the novel CdA/SWCNT nanocomposite coatings not only improves the sensor robustness, but also significantly enhances its sensitivity.

Fig. 17. Comparison between sensitivity and mean response times of the CdA/SWCNTs and SWCNTs based fiber optic sensing configurations obtained for the five tested chemicals.

The bar plots reported in Fig. 17 can be used also to compare the sensing performance of the nanocomposite-based probe with the results obtained with the probe coated by ten monolayers of SWCNTs directly deposited upon the fiber end. It can be clearly observed that the use of the novel CdA/SWCNT nanocomposite coatings not only promotes a better adhesion of the carbon tube to the fiber sensor surface but also significantly enhances the sensitivity of the proposed chemo-optical sensors. As matter of fact, sensor sensitivity from three to seven times higher have been observed for the investigated chemicals with respect to the counterpart optoelectronic sensor directly coated by SWCNTs. However much lower

response times have been obtained in most of the cases, probably due to the fact that the presence of the CdA matrix influences the analyte molecule diffusion times.

5.3 Chemical trace detection in aqueous environments

Once verified their excellent VOC adsorption capabilities in air at room temperature, the sensing characteristics of the CdA/SWCNT nanocomposites have been investigated also for hydrocarbon detection in aqueous environment. To this aim, a fiber optic chemo-sensor coated by 20 monolayers of CdA/SWCNT nanocomposite was exploited for the detection of low concentrations of toluene and xylene in water. In Fig. 18.a have been reported the transient responses of the fiber optic probe as a consequence of several toluene injections with concentrations ranging from 20 to 100 ppm (µl/l). Differently from the air case, a significant reflectance decrease occurred on analyte adsorption within the sensing nanolayer. This could be ascribed to the different SWCNTs-filler content used in this case and, as consequence, to a different refractive index of the sensitive overlay as well as to the dependence of the reflectance on the surrounding refractive index (in accordance with (1) and (2)) combined with the different adsorption characteristics occurring in the two environments. In addition, a good repeatability has been observed in the sensor response when exposed to two successive 100 ppm xylene injections.

Similar results were obtained also in case of xylene detection measurements carried out considering the same concentration range. The calibration curves (reporting the sensor output versus the analyte concentration) are shown in Fig. 18.b. They demonstrate that also for the detection in aqueous ambient a linear dependence exists between the fiber-film reflectance change and the concentration of the two organic analytes.

Fig. 18. (a) Time responses of a sensor coated by 20 CdA/SWCNTs monolayers (75 wt. %) to toluene in water and (b) calibration curves obtained in case of toluene and xylene injections.

In addition, the typical higher affinity of carbon nanotubes-based sensors towards xylene (the sensor sensitivity is $1.0 \cdot 10^{-3} \text{ ppm}^{-1}$) than toluene ($4 \cdot 10^{-4} \text{ ppm}^{-1}$) was confirmed. The sensor resolution obtained in this case are respectively of approx. 0.6 and 1.5 ppm. In addition, to compare the performance of the proposed sensor with those obtained with the one coated by a SWCNT layer, the characteristic curves of the standard SWCNTs-based transducers against toluene in water have also been reported in figure 18.b. The results

clearly reveal that a significant enhancement in the sensor sensitivity can be obtained by the use of SWCNTs-based composite ($4 \cdot 10^{-4}$ ppm⁻¹) with respect to the standard carbon nanotube counterpart ($1.2 \cdot 10^{-4}$ ppm⁻¹).

6. Improving the discrimination ability of SWCNTs-based chemo-sensors

As already discussed in section 4.3, one of the major concerns with chemical sensors is how to improve their discrimination ability among different analytes. In fact, we are still far away from having synthetic and tunable materials able to mimic the tremendous molecular recognition capability of the biological receptors such as enzymes.

Between the two possible approaches typically exploited by the researchers (mentioned in section 4.3) our attention has been focused on the use of sensor arrays composed of low-selective elements combined with pattern recognition algorithms. As matter of fact, in the following we will show the results obtained by applying the PCA on the responses of an array composed of optical chemo-sensors coated by different SWCNTs-based overlays. They will reveal the ability of the photonic sensor array to clearly discriminate among different analytes, either in vapor or gaseous phase.

PCA is a powerful, linear, supervised, pattern recognition technique used as a mathematical tool for analyzing, classifying and reducing the dimensionality of numerical datasets in a multivariate problem (Gardner & Bartlett, 1999). It typically decomposes the primary data matrix (made of a given number of measurements or experimental points) by projecting the multi-dimensional dataset onto a new coordinate base formed by the orthogonal directions with data maximum variance. The eigenvectors of the data matrix are called principal components (PCs) and are uncorrelated among them. The PCs are ordered so that PC₁ displays the greatest amount of variance, followed by the next greatest PC₂ and so on. The magnitude of each eigenvector is expressed by its own eigenvalue, which gives a measure of the variance related to that principal component. As a result of the coordinates change, a data dimensionality reduction to the most significant PCs and an elimination of the less important ones can be achieved without considerable information losses. The main features of PCA analysis are the coordinates of the data in the new base (scores plot) and the contribution to each component of the sensors (loads plot). The scores plot is usually used for studying the classification of the data clusters; while the loads plot can be used for giving information on the relative importance of the sensors to each principal component and their mutual correlation. In this PCA study, the array is composed of the two optical chemo-sensors, coated by ten monolayers of standard SWCNTs and CdA/SWCNTs composite (25 wt.%), whose performance against toluene, xylene, ethanol, isopropanol and NO₂ have been analyzed in section 5.1 (and summarized in Fig. 17). In addition, since we noticed a strong influence of the tested analyte specie on the dynamic behavior of the sensor output (for example the responses to ethanol and isopropanol exhibited a marked overshoot as well as a much faster increase, on exposure, than those to alcohols and NO₂) we applied the PCA both on the static and transient parameters of the response curve (as reported in table 1).

Input data of primary matrix are obtained extracting, for each sensor, the parameters P1-P5 by the responses to different exposures of the five analytes. The PCA was applied to a data-matrix composed by 10 columns (2 sensors x 5 parameters P) and 17 rows (17 measurements x all 5 analytes). Data are further processed by the correlation matrix (centered and standardized data to remove inadvertent weighting that arise to arbitrary units).

	Parameter	Description
P1	$\Delta R/R_0$	Relative reflectance change at the equilibrium
P2	$\Delta R/R_{0_Max}$	Maximum relative reflectance change
P3	$\Delta R/R_{0_3\text{ mins.}}$	Relative reflectance change after 3 minutes
P4	t_{10-90}	Response time
P5	t_{max}	Time needed to reach the maximum $\Delta R/R_0$

Table 1. Parameters extracted from the transient response curve

In Fig. 19 are reported the obtained score plots in the PC1-PC2 and PC1-PC3 planes, revealing that the largest part of information has been reduced to the first PC (60.5%), which is also the most important in the discrimination of the clusters. PC2 comprises a lower amount of information (23.9%) while PC3 only the 8.2%, for a cumulative variance of 92.6%. From score plots it can be seen that NO₂ is the most distinguishable analyte (its samples have the longer distance from those of the other analytes); this can be mainly ascribed to the fact that it is the only one for which both elements of fiber optic sensor array exhibited negative reflectance changes. It also turned out that, the score plot in the plane PC1-PC2 enables one to discriminate between NO₂, ethanol, isopropanol and hydrocarbon in general, since toluene and xylene samples are clustered together. The same occurs for ethanol and isopropanol in the plane PC1-PC3. However, all tested chemicals (either vapors or gas) can be clearly discriminate in the PC1-PC2-PC3 space indicating that this sensor array provides a high discrimination power to these species. This demonstrates that selected features are very powerful for analyte discrimination purposes in the case-study. The results here reported evidence the strong potentiality of the integration of CNTs-based materials with fiber optic technology towards the realization of high-performance SWCNT optoelectronic noses and tongues exploitable for practical environmental monitoring applications.

Fig. 19. PCA score plot of toluene, xylene, ethanol, isopropanol and NO₂ of the data matrix obtained from static and transient responses of CNT-based fiber optic sensors array.

7. Conclusion and future prospects

In conclusion, in this paper the combination of advanced nanostructured coatings based on single-walled carbon nanotubes with the optical fiber technology for the development of high performance opto-chemical sensors has been reviewed. The sensitive material integration has been performed by the customization of the well known molecular engineered Langmuir-Blodgett deposition technique, that has here been used to transfer

ultra-thin layers based on SWCNTs upon the distal end of silica optical fibers. The adopted optical configuration is based on an extrinsic low-finesse Fabry-Perot interferometer, with its principle of operation relying, therefore, on the measurement of the changes in the amount of power reflected at the fiber-film interface occurring as a consequence of the changes in the optical (complex refractive index) and geometrical properties (thickness) of the sensitive elements. Such modifications are, in turn, caused by the interaction of the sensing layers with the target analyte molecules present in the environment.

Since the heart of a chemical sensor is the sensitive layer, from which the main performance of the sensing device derives, a strong effort has been devoted to the investigation of the carbon nanotube overlays features. For this reason, extensive structural and morphological characterizations either of the as-bought SWCNT powders or of the deposited LB SWCNT films have been carried out by means of X-ray diffraction and Raman Spectroscopy analyses, HRTEM and SEM observations. They confirmed the nanostructured dimensions of the exploited class of sensitive material as well as its successful transferring upon the optical fiber surface. The realized chemical sensors have been tested against VOCs and other pollutants either in air or aqueous environments, at room temperature. In most of the investigated cases the fiber optic chemo-sensors coated by SWCNTs demonstrated their strong potentiality as well the ability of detecting environmental pollutants around or well below the ppm threshold. The sensing performance of the proposed opto-chemical probes can be easily tailored by a proper choice of the number of SWCNT monolayers. This choice, however, has to be made by taking account of the trade-off between sensor sensitivity and response time. Furthermore, the use of CdA/SWCNTs-based nanocomposites as novel sensitive nanocoatings has also been presented, revealing their strong potentiality to be successfully employed for chemical sensing both in liquid and gas phase. In addition, preliminary results have been presented demonstrating that it is possible to improve the discrimination ability of SWCNTs-based opto-chemical sensors towards a given chemical specie (thus overcoming their typical poor selectivity) by using standard pattern recognition techniques applied on fiber optic sensor arrays, exploiting both the static and transient features of the single sensor responses.

8. References

- Abdelghani A. and Jaffrezic-Renault N. (2001). SPR fibre sensor sensitized by fluorosiloxane polymers. *Sensors and Actuators B*, 74, 117-123.
- Abdelmalek F., Chovelon J.M., Lacroix M., Jaffrezic-Renault N., Matejec V. (1999). Optical fibre sensors sensitized by phenyl-modified porous silica prepared by sol-gel. *Sensors and Actuators B*, 56, 234-242.
- Adu C.K.W., Sumanasekera G.U., Pradhan B.K., Romero H.E., Eklund P.C.(2001). Carbon nanotubes: A thermoelectric nano-nose. *Chemical Physics Letters*, 337, 31-35.
- Arregui, F. J., Matias I.R., Claus R.O. (2003). Optical Fiber Gas Sensors Based on Hydrophobic Alumina Thin Films Formed by the Electrostatic Self-Assembly Monolayer Process. *IEEE Sensors Journal*. 3, 1, 56-61.
- Azamian B.R. Davis J.J., Coleman K.S., C. Bagshaw C., Green M.L.H. (2002). Bioelectrochemical single-walled carbon nanotubes. *Journal of the American Chemical Society*, 124, 12664.

- Bachtold A., Hadley P., Nakanishi T., Dekker C. (2001). Logic Circuits with Carbon Nanotube Transistors. *Science*, 294, 1317-1320.
- Balasubramanian K. & Burghard M. (2005). Chemically Functionalized Carbon Nanotubes. *Small*, 1, 180-192.
- Baldini F., Chester A.N., Homola J., Martellucci S. (2006). *Optical Chemical Sensors*. NATO Science Series II: Mathematics, Physics and Chemistry, North Atlantic Treaty Organization, Springer, ISBN: 1402046103
- Barone P.W., Baik S., Heller D.A., Strano M.S. (2005). Near-infrared optical sensors based on single-walled carbon nanotubes. *Nature Materials*, 4, 86-92.
- Boisde G. & Harmer A. (1996). *Chemical and Biochemical Sensing with Optical Fibers and Waveguides*. Artech House, Boston, ISBN: 0890067376.
- Brecht A. & Gauglitz G. (1995). Optical probes and transducers. *Biosensors and Bioelectronics* 10, 923-936.
- Chan M. A., Collins S. D., Smith R. L. (1994). A micromachined pressure sensor with fiber-optic interferometric readout. *Sensors and Actuators A*, 43, 1-3, 196-201.
- Chen R.J., Bangsaruntip S., Drouvalakis K.A., Kam N.W.S., Shim M., Li Y., Kim W., Utz P.J., Dai H. (2003). Noncovalent functionalization of carbon nanotubes for highly specific electronic biosensors. *Proc. of the National Academy of Sciences*, 100, 4984-4989.
- Chopra S., McGuire K., Gothard N., Rao A.M., Pham A. (2003). Selective gas detection using a carbon nanotube sensor. *Applied Physics Letters*, 83, 2280.
- Collins P.G., Bradley K., Ishigami M., Zettl A., (2000) .Extreme oxygen sensitivity of electronic. properties of carbon nanotubes. *Science*, 287, 1801-1804.
- Consales M., Campopiano S., Cutolo A., Penza M., Aversa P., Cassano G., Giordano M., Cusano A., (2006_a) .Carbon nanotubes thin films fiber optic and acoustic VOCs sensors: performances analysis. *Sensors and Actuators B*, 118 232-242.
- Consales M., Campopiano S., Cutolo A., Penza M., Aversa P., Cassano G., Giordano M., Cusano A. (2006_b). Sensing properties of buffered and not buffered carbon nanotubes by fibre optic and acoustic sensors", *Measurement Science and Technology*, 17, 1220-1228.
- Consales M., Crescitelli A., Campopiano S., Cutolo A., Penza M., Aversa P., Giordano M., Cusano A., (2007_a) .Chemical Detection in Water by Single-Walled Carbon Nanotubes-based Optical Fiber Sensors. *IEEE Sensors Journals*, 7, 7, 1004-1005.
- Consales M., (2007_b). Carbon Nanotubes Coated Acoustic and Optical VOCs Sensors: Towards the Tailoring of the Sensing Performances. *IEEE Transactions on Nanotechnology*, 6, 601-612.
- Cusano A., Persiano G.V., Russo M., Giordano M. (2004). Novel Optoelectronic Sensing System for Thin Polymer Films Glass Transition Investigation. *IEEE Sensors Journal*, 4, 6, 837-844.
- Cusano A., Pisco M., Consales M., Cutolo A., Giordano M., Penza M., Aversa P., Capodieci L., Campopiano S., (2006_a). Novel Optochemical Sensors Based on Hollow Fibers and Single Walled Carbon Nanotubes. *IEEE Photonics Technology Letters*, 18, 22, 2431-2433.
- Cusano A., Consales M., Cutolo A., Penza M., Aversa P., Giordano M., Guemes A. (2006_b) .Optical probes based on optical fibers and single-walled carbon nanotubes for hydrogen detection at cryogenic temperatures. *Applied Physics Letters*, 89, 201106.

- Dai H. (2002). Carbon nanotubes: synthesis, integration, and properties. *Accounts of Chemical Research*, 35, 1035-1044.
- Dakin J. & Culshaw B. (1988). *Optical Fiber Sensors: Principle and Components*. Artech House, Boston, MA, ISBN: 0890063176.
- D'Amico A. & Di Natale C. (2001). A contribution on some basic definitions of sensors properties. *IEEE Sensors Journal*, 1, 3, 183-190.
- Di Luccio T., Antolini F., Aversa P., Scalia G., Tapfer L. (2004). Structural and morphological investigation of Langmuir-Blodgett SWCNT/behenic acid multilayers. *Carbon*, 42, 5-6, 1119-1122.
- Dresselhaus M. S., Dresselhaus G., Avouris Ph., (2001). *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*. Topics in Applied Physics, Vol. 80, Springer, Berlin, ISBN: 3540410864.
- Fabry C. & Perot A. (1899). Théorie et applications d'une nouvelle méthode de spectroscopie interférentielle. *Annales de Chimie et de Physique*, 16, 115-44
- Fujiwara A., Ishii K., Suematsu H., Kataura H., Maniwa Y., Suzuki S., Achiba Y. (2001). Gas adsorption in the inside and outside of single-walled carbon nanotubes. *Chemical Physics Letters*. 336, 205-211.
- Gauglitz G. (1996). Opto-Chemical and Opto-Immuno Sensors. *Sensor Update*, Vol. 1, VCH, Weinheim.
- Grate J.W. & Abraham M.H. (1991). Solubility interactions and the selection of sorbent coating materials for chemical sensors and sensor arrays. *Sensors and Actuators B*, 3, 85-111.
- Grate J. W. (2000). Acoustic Wave Microsensor Arrays for Vapor Sensing. *Chemical Reviews*, 100, 7, 2627-2648.
- Hartmann J., Auge J. Hauptmann P. (1994). Using the quartz crystal microbalance principles for gas detection with reversible and irreversible sensors. *Sensors and Actuators B*, 19, 1-3, 429-433.
- Heinrich H.K. (1990). Picosecond non invasive optical detection of internal electrical signals in flip-hip-mounted silicon integrated circuits. *IBM Journal of Research and Development*, 34, 162-172.
- Homola J., Yee S. S., Gauglitz G. (2007). Surface plasmon resonance sensors: review. *Sensors and Actuators B*, 54 3-15.
- Huang X.J. & Choi Y.K. (2007). Chemical sensors based on nanostructured materials. *Sensors and Actuators B*, 122, 659-671.
- Iijima S. (1991). Helical microtubules of graphitic carbon. *Nature*, 354, 56-58.
- Jackson D. A. (1994). Recent progress in monomode fibre-optic sensors. *Measurement Science and Technology*, 5, 621-638.
- James D., Scott S.M., Ali Z., O'Hare W.T. (2005). Chemical sensors for electronic nosesystems. *Microchimica Acta*, 149, 1-17.
- James S.W., Tatam R.P. (2006). Fibre optic sensors with nano-structured coatings, *Journal of Optics A: Pure and Applied Optics*, 8, S430-S444.
- Kersey A.D. & Dandridge A. (1990). Applications of Fiber-optic Sensors. *IEEE Transactions on components, hybrid and manufacturing technology*, 13, 1, 137-143.
- Kingery W.D., Bowen H.K., Uhlmann D.R. (1976). in: *Introduction to Ceramics*, Wiley & Sons, New York.

- Kong J., Franklin N.R., Zhou C., Chapline M.G., Peng S., Cho K., Dai H. (2000). Nanotube molecular wires as chemical sensors. *Science*, 287, 622-625.
- Kepley L.J., Crooks R.M., Ricco A.J. (1992). A selective SAW-based organophosphonate chemical sensor employing a self-assembled, composite monolayer: a new paradigm for sensor design. *Analytical Chemistry*, 64, 3191-3193.
- Looney B.B. & Falta R.W. (2000). *Vadose zone Science and Technology Solutions*. Battelle Press, Columbus, OH.
- Lucci M., Regoliosi P., Reale A., Di Carlo A., Orlanducci S., Tamburri E., Terranova M.L., Lugli P., Di Natale C., D'Amico A., Paolesse R. (2005). Gas sensing using single wall carbon nanotubes ordered with dielectrophoresis. *Sensors and Actuators B*, 111-112, 181-186.
- Macleod H. A. (2001). Thin Film Optical Filters, 3rd Edition. *Institute of Physics Publishing*, Bristol and Philadelphia.
- Mignani A.G., Ciaccheri L., Cimato A., Attilio C., Smith P.R., (2005). Spectral nephelometry for the geographic classification of Italian extra virgin olive oils. *Sensors and Actuators B*, 111-112, 363-369.
- Modi A., Koratkar N., Lass E., Wei B., Ajayan P.M., (2003). Miniaturized gas ionization sensors using carbon nanotubes. *Nature*, 424, 171-174.
- Orellana G. (2004). Luminescent optical sensors. *Analytical and Bioanalytical Chemistry*, 379, 3, 344-346.
- Penza M., Antolini F., Vittori Antisari M. (2004_a). Carbon nanotubes as SAW chemical sensors materials. *Sensors and Actuators B*, 100, 47-59.
- Penza M., Cassano G., Aversa P., Antolini F., Cusano A., Cutolo M., Giordano M., Nicolais L. (2004_b). Alcohol detection using carbon nanotubes acoustic and optical sensors. *Applied Physics Letters*, 85, 12, 2379-2381.
- Penza M., Cassano G., Aversa P., Antolini F., Cusano A., Consales M., Giordano M., Nicolais L. (2005_a). Carbon nanotubes-coated multi-transducing sensors for VOCs detection. *Sensors and Actuators B*, 111-112, 171-180.
- Penza M., Cassano G., Aversa P., Cusano A., Cutolo M., Giordano M., Nicolais L. (2005_b). Carbon nanotube acoustic and optical sensors for volatile organic compound detection. *Nanotechnology*, 16, 2536-2547.
- Penza M., Cassano G., Aversa P., Cusano A., Consales M., Giordano M., Nicolais L. (2006_a). Acoustic and Optical VOCs Sensors Incorporating Carbon Nanotubes. *IEEE Sensors Journal*, 6, 4, 867-875.
- Penza M., Tagliente M.A., Aversa P., Cassano G., Capodieci L. (2006_b). Single-walled carbon nanotubes nanocomposite microacoustic organic vapor sensors. *Materials Science and Engineering C*, 26, 1165-1170.
- Penza M., Tagliente M.A., Aversa P., Re M., Cassano G. (2007_a). The effect of purification of single-walled carbon nanotube bundles on the alcohol sensitivity of nanocomposite Langmuir-Blodgett films for SAW sensing applications. *Nanotechnology*, 18, 185502.
- Penza M., Aversa P., Cassano G., Wlodarski W., Kalantar-Zadeh K. (2007_b). Layered SAW gas sensor with single-walled carbon nanotube-based nanocomposite coating. *Sensors and Actuators B*, 127, 168-178.
- Riu J., Maroto A., Rius F.X. (2006). Nanosensors in environmental analysis. *Talanta*, 69, 288-301.
- Roberts G. (1990). *Langmuir-Blodgett Films*. Plenum Press, New York ISBN: 0306433168.

- Saito R., Dresselhaus G., Dresselhaus M.S. (1998). *Physical Properties of Carbon Nanotubes*. Imperial College Press, London, ISBN: 1860942237.
- Soref R. & Bennet B.R. (1987). Electrooptical effects in Silicon. *IEEE Journal of Quantum Electronics*, 23, 123-129.
- Sotiropoulou S., Gavalas V., Vamvataki V., Chaniotakis N.A., (2003). Novel carbon materials in biosensor systems. *Biosensors and Bioelectronics*, 18 (2003) 211.
- Steinberg I.M., Lobnik A., Wolfbeis O.S., (2003). Characterisation of an optical sensor membrane based on the metal ion indicator Pyrocatechol Violet. *Sensors and actuators B*, 90, 230-235.
- Sumanasekera G.U., Adu C.K.W., Fang S., Eklund P.C., (2000). Effects of gas adsorption and collisions on electrical transport in single-walled carbon nanotubes. *Physical Review Letters*, 85, 1096-1099.
- Sumanasekera G.U., Pradhan B.K., Romero H.E., Adu C.K.W., Foley H.C., Eklund P.C. (2002). Thermoelectric Chemical Sensors Based on Single-walled Carbon Nanotubes. *Molecular Crystals and Liquid Crystals*, 387, 31-37.
- Takamoto D.Y., Aydil E., Zasadzinski J. A., Ivanova A.T., Schwartz D.K., Yang T., Cremer P.S. (2001). Stable Ordering in Langmuir-Blodgett Films. *Science*, 293, 5533, 1292-1295.
- Terrones M. (2003). Science and technology of the twenty-first century: Synthesis, Properties, and Applications of Carbon Nanotubes. *Annual Review of Materials Research*, 33, 419-501.
- Wei B.Y., Lin C.S., Lin H.M. (2003). Examining the Gas-Sensing Behaviors of Carbon Nanotubes Using a Piezoelectric Quartz Crystal Microbalance. *Sensors and Materials*, 15, 177-190.
- Wilson L.G., Everett L.G., Cullen S.J. (1995). *Handbook of Vadose Zone Characterization & Monitoring*. CRC Press, Boca Raton, FL, ISBN: 0873716108.
- Wolfbeis O.S. (2004). Fiber-optic chemical sensors and biosensors. *Analytical Chemistry*, 76, 3269-3284.
- Wolfbeis O.S. (1991). *Fiber Optic Chemical Sensors and Biosensors. Vol. II*, CRC Press, Boca Raton ISBN: 0849355095.
- Wooten F. (1972). *Optical Properties of Solids*, Academic Press, New York, ISBN: 0127634509.
- Yoo S., Jung Y., Lee D.S., Han W.T., Oh K., Murakami Y., Edamura T., Maruyama S. (2005). Optical anisotropy in single-walled carbon nanotubes. *Optics Letters*, 30, 3201-3203.
- Zahab A., Spina L., Poncharal P., Marliere C. (2000). Water-vapor effect on the electrical conductivity of a single-walled carbon nanotube mat", *Physical Review B*, 62, 10000.
- Zarcomb S. & Stretter J.R. (1984). Theoretical basis for identification and measurement of air contaminants using an array of sensors having partially overlapping sensitivities. *Sensors and Actuators*, 6, 225-243.
- Zhang J., Hu J., Zhu Z.Q., Gong H., O'Shea S.J., (2004). Quartz crystal microbalance coated with sol-gel-derived indium-tin oxide thin films as gas sensor for NO detection. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 236, 1-3, 23-30.
- Zhao Q., Frogley M.D., Wagner H.D. (2002). Direction-sensitive stress measurements with carbon nanotube sensors. *Polymers for Advanced Technologies*, 13, 10-12, 759-764.
- Zudans I., Heineman W.R., Seliskar C.J. (2004). In situ measurements of chemical sensor film dynamics by spectroscopic ellipsometry. Three case studies. *Thin Solid Films*, Vol. 455-456, 1, 710-715.

Optical Fiber New Developments

Edited by Christophe Lethien

ISBN 978-953-7619-50-3

Hard cover, 586 pages

Publisher InTech

Published online 01, December, 2009

Published in print edition December, 2009

The optical fibre technology is one of the hot topics developed in the beginning of the 21st century and could substantially benefit applications dealing with lighting, sensing and communication systems. Many improvements have been made in the past years to reduce the fibre attenuation and to improve the fibre performance. Nowadays, new applications have been developed over the scientific community and this book fits this paradigm. It summarizes the current status of know-how in optical fibre applications and represents a further source of information dealing with two main topics: the development of fibre optics sensors, and the application of optical fibre for telecommunication systems.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Marco Consales, Antonello Cutolo, Michele Penza, Patrizia Aversa, Michele Giordano and Andrea Cusano (2009). Fiber Optic Chemical Sensors Based on Single-Walled Carbon Nanotubes: Perspectives and Challenges, Optical Fiber New Developments, Christophe Lethien (Ed.), ISBN: 978-953-7619-50-3, InTech, Available from: <http://www.intechopen.com/books/optical-fiber-new-developments/fiber-optic-chemical-sensors-based-on-single-walled-carbon-nanotubes-perspectives-and-challenges>

INTech
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2009 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen