

APPLYING ODDS OF NANOTECHNOLOGIES FOR ENVIRONMENTAL IMPACT ASSESSMENT

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ABSTRACT: *The issue regarding environmental impact assessment has started to be debated more than 50 years ago, as diverse impacts on environment because of different human economic activities especially industrial ones have been remarked. By this was more than clear that technological advance brings not only positive desired impacts for human society but negative unwanted ones as well, especially because of environmental pollution. Such issues have been debated during the Conference for Environment in Stockholm 1972 and emphasized in the first report to the Club of Rome „Limits of Growth“, published in the same year. As a direct result of the recognized state, discussions have globally been carried out in order to try finding adequate solutions to created situation. In this context the concept of Sustainable Development has emerged after engaged debates and has been defined 1987 in the Brundtland Report of the World Commission on Environment and Development. This means that technical, economic, as well as environmental and social systems have to be holistically considered by simultaneously approaching physical, chemical, biological, economic and social processes. Environmental impact assessment has to be carried out especially because of registered advances in technological field combined with the field of physics, bringing by this new developments in nanotechnology field, fact that emphasizes diverse applying odds in environmental field. Applying carbon nanotubes, CNTs for environmental impact assessment means designing environmental sensors for environmental monitoring.*

Keywords: *environmental monitoring, environmental impact assessment, nanotechnology, environmental sensors, carbon nanotubes, CNTs, multidisciplinary, sustainable development*

1. Introduction

Starting with the seventies can be stated the beginning of undesired impacts recognition on environment because of carried out economic activities especially industrial ones besides their positive intended effects on human society. In the last half of a century several events have been organized on global, national, and local level to debate complex existing challenges and to

try finding suitable solutions for created provocations. The Conference for Environment, which took place 1972 in Stockholm and the first report to the Club of Rome „Limits to Growth“, published in same year have represented best occasions to start debates concerning emerged challenging situation, that besides wanted impacts of technological advance, unwanted effects are also appearing [24].

Currently humanity is confronting itself with global challenges, which can be divided

in three groups, as follows: growth of world population, increase of energy and natural resources consumption and environmental pollution, as emphasized in Figure 1. Debates that followed on scientific, political, and social levels have had as a central goal to state potential solutions for the challenges shown above, which could be applicable to developed as well as to developing countries with respect to regional differences [16].

Results of the multitude of global debates have been put together in the Brundtland Report of the World Council on Environment and Development, released 1987, defining for the first time the concept of sustainable development [8]. Emerged concept of sustainable development was worldwide accepted as being actually the proper answer for the complex environmental, technological, economic and social challenges on global level. Nevertheless it has to be stated that this concept was pretty much discussed 1992 during the Conference for Environment and Development in Rio de Janeiro, having had the „Agenda 21“ as main output of this conference. Ten years later took place 2002 the follow-up conference called as „Rio + 10“ - Conference in Johannesburg as well as in 2012 the so-called „Earth Conference“ for Sustainable Development, known as „Rio + 20“ - Conference, this time again in Rio de Janeiro [48].

2. Environmental Impact Assessment for Sustainability

On global level debates began on scientific, social, and political level for finding best solutions for arisen challenges, which could be applicable with respect to regional differences to the developed as well as to the developing countries. In this context several concepts for the proper development of humanity have been discussed in the past, emphasizing potential danger because of potential negative impacts on environment by pollutants emissions in

the air, water and soil. When assessing technologies several criteria are needed, usually quantified by environmental indicators, which to point out the environmental quality. Corresponding activities regarding evaluating technologies can be best sustained by the newer subject called Technology Assessment, TA, that allow working in inter- and multidisciplinary way, connecting by this different subjects form different fields. [6, 16, 29, 37, 42]. Although in the last 20 years lot of progress was been registered in the field of technology assessment especially due to several studies carried out in USA, Japan, Germany and other European countries, there is still need in developing integrative methods for technology assessment [16, 38].

Carrying out environmental impact assessment studies is actually representing a basic condition for assuring the sustainability of our human society. The Brundtland Report of the World Council on Environment and Development, released 1987, represented a result of engaged worldwide debates, defining for the first time the much debated concept of sustainable development, as representing the right answer to complex ecological, economic, and social problems on global level, as emphasized in Fig. 1: *“Sustainable development means the ability of humanity to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs”* [8].

Scientific literature is pointing out two strategic possibilities for applying the concept of sustainable development on different levels [6, 37, 50]:

- stating goals on global or national level, appropriate measures to get these goals being prepared on global or national level and applied on regional level
- stating goals on regional level, appropriate measures being prepared on regional or local level, their potential effects being assessed on national and global level too.

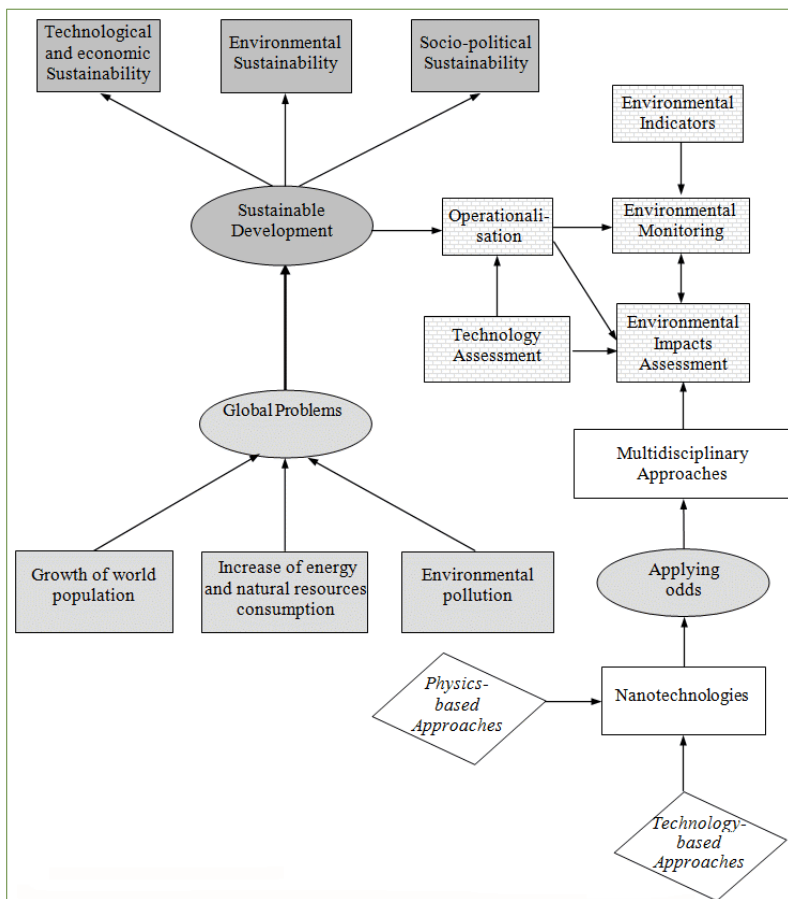


Fig. 1. Nanotechnologies Applying Odds for Environmental Impact Assessment in Sustainable Development Operationalisation

Studies containing diverse scenarios, for instance with the goal of finding future sustainable energy supply systems with minimum environmental impacts by using renewable energies, can be mentioned as application example of the first strategy. Second strategy is related to different initiatives in form of Local Agendas 21, firstly carried out in Western European countries after the Rio - Conference 1992, later also in Eastern European countries as well as in other countries in the world. Also studies concerning regional future energy supply systems by considering potential impacts can be mentioned, pointing out advantages of using renewable energy resources [16, 39].

Sustainable development can be operationalised by considering Technology Assessment, as presented in Figure 1 [42]. Concretely applying the concept of sustainable development is possible, when for an individual problem-case specific goals are defined and concepts to get these goals are developed [16, 37]. Sustainability is anyway to be defined for each different situation by clearly stating space and time scales, where studies for environmental impact assessment are becoming very relevant in this regard, needing environmental monitoring by using newer modern technical applications in this regard, as by applying nanotechnologies, especially carbon nanotubes, CNTs [12, 30]. After

carrying out specific monitorisation by collecting data and calculating specific indicators and by comparing them to existing reference values, conditions are got to successfully carry out environmental impact assessment and management [16, 38, 49].

From Figure 1 can be observed that a main role in the context of operationalising sustainability is taken by environmental aspects. Being more specific the role of environmental indicators is very relevant when taking into account environmental quality. In order to point out specific aspects regarding environmental impact assessment and by this environmental quality, a first step in this regard is represented by carrying out environmental monitoring, modern tendencies emphasizing the possibility of applying nanotechnologies, especially carbon nanutubes in this regard [30].

3. Environmental Monitoring

As it is presented in Figure 1, the issue of applying sustainable development means actually translating its goals into different strategies, and these ones into concrete measures to be applied in several fields, as technological, economic, environmental, and social field. In order to succeed verifying developments intended to be got, especially in environmental field, there is a need to elaborate singular controlling instruments in form of indicators, i.e. environmental indicators, which have to support environmental impact assessment by environmental monitoring [29]. In this context environmental sensors are representing the main instrument by which environmental monitoring can be carried out. Environmental sensors, or more general sensors, are linked objects, having the capacity to provide various types of information, depending on their properties, such as location, position, velocity, and data collected for certain environmental pollutant elements, depending on their specific designed role [12, 30].

Worldwide there have been and still there are many attempts for developing and establishing flexible adaptive systems for environmental monitoring on different levels. As it is known, an important part of environmental monitoring systems is represented by environmental indicators, which can be simple or more complex ones, by aggregating various single environmental variables and parameters [37]. In order to design appropriate environmental indicators depending on existing targets, as well as depending on the considered level, there is a need to take into account most relevant environmental variables, for which measurements can also be carried out in certain time intervals [16].

An accomplished model regarding environmental indicators is the pretty well known pressure-state-response model [4]. Going into details, there are about 60 indicators in this model for the pressure, state, and response part. On the other side, in the meantime there is also a structural classification of environmental indicators in specific, composite and key indicators. Going into details a lot of environmental indicators for emphasizing air, water or soil pollution have been designed and are nowadays applied in many countries [1, 38].

For assessing environmental quality in a certain region of interest there is a need to carry out environmental monitoring by using certain indicators for describing air, water or soil quality. To be more concrete, in order to carry out environmental monitoring several measurements of singular environmental variables and parameters have to be carried out in the first stage. In order to make specific environmental measurements there is a need to use with this goal proper measuring devices, as it is emphasized in Figure 2, for finally drawing conclusions regarding environmental quality in the analysed region [1, 16]. Such measuring devices in environmental field are mostly based on different environmental sensors, which have the capacity to detect and

emphasize the existence of certain pollutants, for which they have been designed to detect and measure [1, 30].

Anyway at high pollutant concentrations the signal from the pollutant is strong enough, although interfering effects can influence it

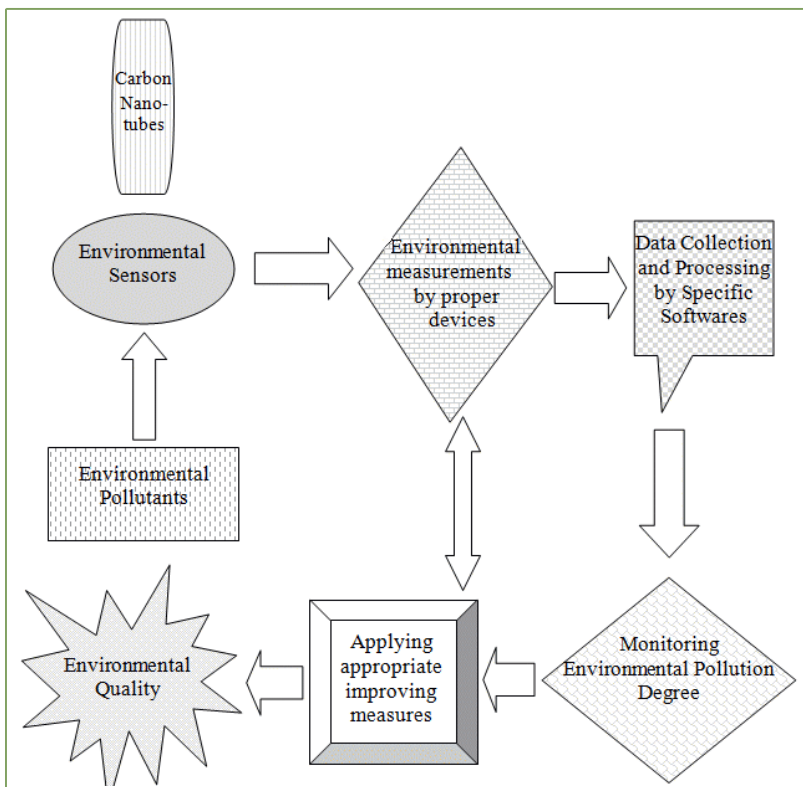


Fig. 2. Environmental monitoring by environmental sensors based on Carbon Nanotubes

As mentioned before, environmental sensors are linked objects capable of providing various types of information, depending on their types and properties. There are several categories of sensors currently available [30]. For instance electrochemical sensors are based on a chemical reaction between gases in the air and the electrode in a liquid inside a sensor. Developing such sensors is a pretty difficult process, as signals from sensors not only depend on the air pollutant of interest, but they can be influenced by several factors. Such factors can be interfering compounds, temperature, humidity, pressure and signal drift.

pretty strong [7].

Measurements results made by sensors strongly depends on applied technology as well as on concrete implementation, meaning by this the application, site, conditions, as well as set-up [30]. This is the argument why sensor outputs at different measurement sites can often differ [7]. Anyway due to the influence of meteorological parameters on the sensor signal, correction is in more of the situations not even possible. Nevertheless, the measurement uncertainty of these devices is often neglectible compared to made advance by detecting real pollution rates in considered situation [7].

4. Environmental Sensors by Carbon Nanotubes

Carbon nanotubes (CNTs), since their first discovery by Iijima in 1991 [13], can be found in many applications due to their unique geometry, morphology and properties. Their potential applications include gas storage and separation, sensors, and fuel cells [9, and 13], as well as being mostly used to fabricate field emission emitters, as we have conducted several research work in this field with a view to developing new electron sources of this type [19, and 25-28]. Carbon nanotubes belong to the family of fullerene structures. There are two types of nanotubes [13]:

- single walled carbon nanotubes (SWCNTs). A SWCNT can be considered as a one-atom thick layer of graphite rolled up into a seamless cylinder with a diameter of several nanometers, and length on the order of 1–100 microns.
- multiwalled carbon nanotubes (MWCNTs). MWCNTs consist of multiple layers of graphite wrapped up together to form a tube shape, sharing the same central axis.

In the last few years, different studies have shown the excellent potential of CNTs as sensitive material for detecting chemical molecules and biological. Via a functionalisation of CNT sidewalls, a better chemical bonding between a specific functional group and the nanotube can be reached and the selectivity of the adsorption process can be enhanced [20]. Some properties of CNTs make them very attractive to produce small, wearable sensors for environment monitoring and protection, risk prevention, agriculture and even in food, and chemical industries [47]:

- Their intrinsic strength makes them suited for miniaturised sensors and usable on flexible substrates.
- They respond even operated at room temperature, which is optimal for

ultra-low power, wearable, battery-operated devices. Such devices could easily meet the requirements of intrinsically safe operation, needed in environment protections where the occurrence of flammable/explosive atmospheres is possible.

- Once functionalised, the adsorption of a small quantity of chemical species can result in a dramatic change of the CNT conductivity. Therefore, CNT are suited to detect species at low concentrations (e.g. low parts per billion (ppb) level).
- A sensor can be built using a simple transducer to monitor the electrical resistance of a CNT-based film.

Environmental sensors based on CNTs are devices used in areas where the control and analysis of (anomalous) substances are necessary: a transduction system, which allows the detection and quantification of (anomalous) substances in many different environments. Gas sensors based on CNTs have been attracting intensive research interest due to the demand of sensitive, fast response, and stable sensors for air monitoring and protection. There is a wide range of gas sensors based on CNTs (as active layer), which measure the resistance or conductivity change of the active layer upon adsorption of gas molecules [44]:

Gas sensors based on pristine CNTs.

Using the interaction of NO₂ as example, [5] reported that gas adsorption within pristine CNTs can occur in four distinct sites: (1) the external surface of the bundle, (2) the groove formed at the contact between adjacent tubes on the outside of the bundle, (3) the interior pore of individual tubes and (4) interstitial channel formed between adjacent tubes within the bundle. They also found that upon exposure to toxic gases such as NO₂, NH₃, and CO, the electrical conductance of semiconducting CNT changes, even when they are operated at low temperatures, thus considerably reducing the power consumption of the sensing device.

Gas sensors based on plasma functionalized CNTs. This treatment, in addition to the better dispersion sought, gives rise to functional groups attached to the surface of the nanotubes, which modifies the CNT-surface reactivity and can further improve gas detection. Most of the previous reports are based on utilization of carboxylic acid ($-\text{COOH}$) groups grafted on the surface of CNTs, which provide reactive sites for interacting with different compounds [11, and 14]. [11] reported that the $-\text{COOH}$ group grafted on MWCNTs provides reactive sites via esterification or elimination, and the MWCNTs retain the graphitic structure. It also showed that their sensors have proved to give good results when operated at ambient temperature, above all showing good responsiveness to low concentrations of NO_2 . [14] used plasma functionalized MWCNTs for the detection of NO_2 and NH_3 . They were able to detect them at 500 ppb and 200 ppm respectively with good sensitivities. By increasing the oxygen plasma treatment time, the amount of $-\text{COOH}$ groups on the surface of the nanotubes increased, resulting in an increased sensitivity to the tested gases.

Gas sensors based on metal decorated CNTs. As an extension of the usual functionalisation techniques, CNT can be decorated with metal nanoparticles. Since metal nanoclusters show a wide range of advanced physicochemical properties (e.g. high catalytic activity, adsorption capacity, efficient charge transfer, etc.), they can provide a full range of reactivity towards different gases [35]. [18] demonstrated room-temperature detection of H_2 when carbon nanotubes were functionalized by Pt or Pd nanoparticles. Those metals act as catalysts for the adsorption of H_2 . In this way, Pd- or Pt-CNTs became very sensitive to H_2 , while pristine ones did not show any response to that gas. In fact, hydrogen molecules dissociate into atomic hydrogen on Pt surfaces and form PtH, which will lower the work function of Pt and cause the

electron transfer from Pt to MWCNTs [31]. [36] proposed a mechanism for the detection of hydrogen using Pd/SWCNTs. They suggested that when the Pd decorated semiconducting SWNTs are exposed to hydrogen, the Pd atoms are converted to palladium hydride (PdH), which possesses a lower work function than that of pure Pd. As a result, the formation of PdH is beneficial to the accumulation of more electrons around the carbon atoms of the SWNTs. The higher level of accumulation of electrons around the carbon atoms further decreases the valence band energy level, leading to a sensitive decrease of the conductance of the SWNTs. The Pd-CNTs are also sensitive to CH_4 , with enhanced sensitivity, reduced size and power consumption compared to conventional metal oxide gas sensors [23]. [21] reported a composite of MWCNTs/Pd prepared by a facile method of chemical reduction. It exhibited a reversible and reproducible response magnitude of 4.5% toward 2% CH_4 at room temperature. The response and recovery times were estimated to be 310 seconds and 176 seconds, respectively. The inert CH_4 does not undergo a charge transfer reaction with the MWCNTs to initiate a change in the electrical properties of CNTs, so MWCNTs alone are insensitive to methane. In the composite, the palladium nanoparticles undergo a weak interaction with the CH_4 molecules adsorbed on the composite to form a long-range weakly-bound complex at room temperature. The MWCNTs donate electrons to Pd to promote the formation of the complex where CH_4 is electronegative. The hole density in the MWCNTs is thus increased, resulting in a higher current in the composite. [32] presented Au and Pt nanocluster functionalized MWCNTs chemiresistive sensors for detecting NO_2 and NH_3 working at a temperature range of 100–250°C. Au, and Pt nanoclusters were sputtered on the surface of MWCNTs. The gas response of Pt- and Au-functionalized MWCNT gas sensors was significantly improved by a factor up to

an order of magnitude for NH₃ and NO₂ detection, respectively. The enhancement of the gas response of the metal modified MWCNT sensors could be caused by a combination of two additional effects of (1) direct charge injection and (2) catalytically induced charge into functionalized MWCNTs. The importance of the size of metal nanocluster in the reactivity of the hybrid materials towards gases has been studied. In fact, it is known that small size clusters lead to a stronger interaction with gases. However, [33] studied the effect of three different Au nanocluster sizes on the performance of Au/MWCNTs towards H₂S, NH₃ and NO₂. They found the existence of a critical size in which the interaction is maximum. They, suggested that small size particles around 2.5 nm showed a tendency to agglomerate leading to sensitivities close to those obtained for bigger nanocluster sizes of about 10 nm. In contrast, 5 nm nanoparticles gave the best results. These particles remained isolated on the external wall of nanotubes, which explains the improved sensitivity to gases shown by this material.

Gas sensor based on metal oxide doped CNTs. Recently, hybrid films based on tin or tungsten oxide and carbon nanotubes have been introduced as new gas-sensitive materials with improved sensitivity [3]. This work indicated that the detection at ambient temperature of toxic gases such as nitrogen dioxide, carbon monoxide and ammonia or ethanol vapors can be improved by dispersing an adequate quantity of carbon nanotubes into a metal oxide matrix. A model was presented to relate potential barriers to electronic conduction in the hybrid material. This model suggested that the high response is associated with the stretching of the depletion layers at the grain boundaries of SnO₂ and the SWCNTs interfaces when detected gases are adsorbed. [10] fabricated a NH₃ sensor with a composite of SWCNTs and SnO₂. The sensor could detect the concentration of NH₃

down to 10 ppm at room temperature, and exhibited a fast response time of 100 seconds and recovery time of about 3.2 minutes. The SWCNTs in the matrix of SnO₂ provide the main conducting channel that effectively varies in its conductance upon adsorption of NH₃. The recovery time depends on the bonding force of NH₃ molecules to the SWCNT surface with respect to desorption under a nitrogen flow. Thus, it can vary with the nitrogen flow rate. In [41], the response of the MWCNTs/SnO₂ sensor to NH₃ increases with increasing MWCNTs content and the composites using MWCNTs with the larger diameter show higher response because larger diameter MWCNTs would increase the number of gas molecules adsorbed on the material. In [22], hybrid sensors containing MWCNTs respond at significantly lower operating temperature than their non-hybrid counterparts. These new hybrid sensors show a strong potential for monitoring traces of oxygen (i.e., <10 ppm) in a flow of CO₂. The heterostructure n-TiO₂/p-MWCNTs can be formed at the interface between titania and carbon nanotubes. Hybrid sensors are significantly more responsive to oxygen than pure or Nb doped titania sensors because a slight change in the concentration of adsorbed oxygen at its surface can result in a significant change in the depletion layer at the n-TiO₂/p-MWCNT hetero-structure. A ZnO/MWCNT sensor was implemented recently. It showed better sensing performance when compared to bare MWCNTs. The former allows for the discrimination of low CO concentrations (20, 50 and 200 ppm) which is important for several practical applications [17].

Gas sensor based on Nitrogen or Boron doped CNTs. The incorporation of nitrogen or boron atoms into the honeycomb lattice leads to chemical activation of the rather passive surface of a carbon nanotube and adds additional electronic states around the Fermi level. Nitrogen or boron introduction to CNTs significantly modifies their physical

and chemical properties, notably changing their solubilities and increasing surface reactivity [14]. Although pristine carbon nanotubes show good sensitivity to oxygen, they often show little response to pollutant gases such as NO₂, as supported by theoretical modelling showing only weak surface-gas interaction [40]. The modification of states in N- or B-doped tubes suggests that their interaction with absorbing gas species and resultant transport properties should also be modified, and thus doped nanotubes appear in principle as promising candidates for gas sensing purposes. N- or B-CNTs should show significant advantages over undoped nanotubes for gas sensor applications, both due to their reactive tube surfaces, and the sensitivity of their transport characteristics to the presence, distribution and chemistry of nitrogen and boron. [2] first performed calculations suggesting that N-CNT may be useful in gas sensing for CO₂ and H₂O, due to the ability of nitrogen dopants to bind to incoming gas species. [43] proved the concept introduced by [2] by investigating the conductivity of both aligned N-CNT films and N-CNT compressed pellets with various gases (NH₃). Both chemisorption (permanent conductance change) and physisorption (transient conductance change) was observed, depending on the species. The films showed moderate sensitivities (i.e. the gases were tested at very high concentrations ranging from 1% up to 16%). Despite their moderate sensitivity towards the species tested, N-CNT films were found to be more efficient than un-doped CNT films for detecting toxic gases. This was attributed to the presence of highly reactive pyridine-like sites on the surface of N-CNTs. Using abinitio calculations, they confirmed that pyridine-type regions on the tube surface bind strongly to ammonia, acetone and hydroxyl groups, thus altering the tube density of states. [44] studied intrinsic and B atom, N atom and BN atoms doped singlewalled carbon nanotubes (SWCNTs),

as sensors to detect hydrogen sulfide, using density functional theory (DFT). The calculated results show that the B-doped SWCNTs present high sensitivity to the gaseous hydrogen sulfide molecule, and their geometric structures and electronic properties present dramatic changes after the adsorption of H₂S molecule, compared with the intrinsic SWCNTs. While N-doped SWCNTs and BN-doped SWCNTs cannot improve the sensing performance of the SWCNTs to H₂S molecule. So it is suggested that B-doped SWCNTs would be promising candidates for serving as effective sensors to detect the presence of H₂S molecules.

Gas sensor based on polymer coated CNTs. Among the organic polymers, conducting polymers are promising materials for gas sensing as they have delocalized bonds that make them semiconducting or even highly conductive. Several conducting polymers, for example, polyaniline, polypyrrole, polythiophene have been demonstrated to be good sensing materials to function at room temperature. They have been applied as conductometric, potentiometric, amperometric and voltammetric transducers for the detection of a wide variety of gas or vapors such as NH₃, NO₂, and CO [47]. However, their selectivity and the environmental stability are poor. Recently, enhanced gas sensing by combining SWCNTs with organic polymers has been demonstrated. [34] showed that noncovalently drop coating of polyethyleneimine (PEI) and Nafion (a polymeric perfluorinated sulfonic acid ionomer) onto SWCNTs FETs resulted in gas sensors with improved response and selectivity for NO₂ and NH₃. The PEI functionalization changed the SWCNTs from p-type to n-type semiconductors. Chemical functionalization of SWCNTs with covalently attached poly-(m-aminobenzene sulfonic acid) (PABS) has been demonstrated to result in better sensing performance toward NH₃ and NO₂ than simply carboxylated SWCNTs. Sulfonic acid groups

as dopants play an important role in balancing the charge distribution within the polymer, and they are especially attractive for introducing acidbase response.

A recent review about gas sensors based on CNTs proposed a good summary about the sensing performances of pristine, metal functionalized, metal oxide doped CNTs sensors reported up to 2009. From this review, it was observed that carbon nanotubes have been extensively studied as gas sensors. Pristine carbon nanotubes based gas sensors were able to detect some gases at room temperature. This detection, such in the case of NO₂ is mainly due to chemisorption. Since carbon nanotubes behave like graphite at room temperature, the chemisorptions must be attributed to the defects formed in the carbon nanotubes during their post fabrication or post purification step. This has lead scientists to work in the idea of functionalizing the CNTs via creating oxygenated defects or decorating them with metals and metal oxides, polymers, etc. From the reviwie, it was seen that thanks to functionalization, the range of detectable gases either using SWCNTs or MWCNTs was increased, the detection limit was decreased down to ppb levels, response time was decreased to some seconds and recovery time to some minutes thanks to heating, illumination or using higher carrier gas flows [46].

5. Conclusions

In the context of developing and using different technological applications the operationalisation of sustainable development means carrying out technology assessment studies especially environmental impact assessments.

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Registered environmental impacts associated with different economic activities have increased the general interest of scientists for using and developing specific methods of technology assessment, where inter- and multidisciplinary approaches are of great interest.

To assure getting small environmental impacts because of using diverse technological applications in our daily life, early monitoring of pollutants is of foremost importance.

Newer scientific odds in this regard have been made possible with the development of nanotechnology field. When considering nanotechnologies for environmental impact assessment especially carbon nanotubes define in this context new application odds for environmental monitoring. Most of the known traditional analytical methods have disadvantages such as high costs, considerable time requirements, off-site determination, and technical training. From made presentation it became clear that CNT-based sensors are of great interest due to small sizes, low costs, capability for on-site determinations, high sensitivity, and selectivity, as well as fast response time. Advances in the field of applying CNTs will with sure play a main role in evolving such a technology.

By using CNTs there is a hope with regard to development of new modern sensor methods. As a conclusion of made remarks, it is to be expected that CNTs-based environmental sensors will start to be successfully applied in diverse environmental monitoring systems for emphasizing pollution challenges and for supporting by this the development of new modern environmental protection technologies.

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Abbreviations:

CNT – Carbon Nanotube