

Environmental Sensors through Nanomaterials

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Abstract

For the safe Environmental it is required the measurement and detection of the constituents of soil, water and air. Nanomaterials offer unique properties that can be exploited in novel environmental sensors. We consider both inorganic and organic materials that are synthesized as spherical particles, tubes, rods, belts and wires. The electrical, magnetic, chemical and optical properties of these materials are used to detect the presence of environmental toxins or other undesirable vapors or liquids at the particle's surface. We review the application of nanomaterials to sensors & include a discussion of physical gas sensors that are based on nano-scale materials.

Keywords: Nanoparticle, FCC, ITO, Biosensor, Gas Sensors,

1. Introduction

Environmental science and technology frequently require the measurement and detection of the constituents of soil, water and air. Measurements of these components of the environment are often necessary first steps in the development and validation of models of environmental processes. Measurements are also very important during the monitoring of processes in the environment, particularly with regard to monitoring the transport of contaminants, and detection of toxins like pesticides. Air quality modeling requires high quality data on the concentrations of air contaminants. Typical components of the air of interest are those compounds that are often emitted by combustion sources such as engines. The air pollution that is created from these emissions is well-known to have an adverse impact on health[1,2]. Gas phase species such as carbon monoxide, unburned hydrocarbons, oxides of nitrogen, ozone, and most significantly in recent times, particulate matter, are known to be associated with adverse effects on human health. Over the years, many bench-top analyzers have been developed for detecting these compounds in the ambient air. Those technologies are well established but the instruments are fairly large and expensive.

Their size and cost do not permit the deployment of such systems in large-scale arrays of sensors. The thrust of recent sensor research is directed towards the development of smaller, cheaper, portable devices. The detection of toxins in ground water and in soil is very important in assessing threats to human health from seepage of waste from contaminated soils, and in monitoring the transport of toxins through the ground water and eventually consumption by humans. In general, well-established techniques such as liquid and gas chromatography are used to analyze samples that are returned to the laboratory. This method of analysis is slow and expensive. It is certainly not amenable to the deployment of large-scale arrays for detecting the transport of toxins from contaminated sites. The materials may be widely dispersed, as is the case with dioxins. The detection of trace compounds in the environment faces problems that are unique to environmental science and technology. First, the detection must take place within a complex matrix of many compounds, all of which may interfere with the detection process. Oxygen, which is generally ubiquitous in environmental settings, can interfere with measurements by quenching fluorescence. Sensors that are based on immuno assay techniques, that typically use antibodies as bio-recognition elements, can also suffer from interference from other compounds in the sample due to non-specific binding[3].

2. Nanoscale Materials for Sensors

2.1 Quantum Dots

Quantum dots (QDs) represent an early implementation of optically-active nanoscale materials. They are made of semiconductor materials with electrons that have energy levels typical of the particular semiconductor material. The exciton Bohr radius represents the average physical separation between excited electron-hole pairs for each material. If the size of a semiconductor crystal becomes as small as the size of the material's exciton Bohr radius, then the electron energy levels become

discrete. This phenomenon is called quantum confinement and under such conditions the material is termed a quantum dot. Due to the quantum confinement effect, the absorbance peak of quantum dots and their emission maxima shift to higher energies (shorter wavelengths) with decreasing particle size [3]. Since "naked" QDs are susceptible to photo-oxidation, they need to be capped by a protective shell of an insulating material or wide-bandgap semiconductor, structurally matched with the core material. Core-shell geometries where the nanocrystal (typically from 2 to 8 nm in diameter) is encapsulated in a shell of a wider band gap semiconductor have increased fluorescence quantum efficiencies (>50%) and greatly improved photochemical stability. The emission quantum yield of these particles increases with increasing thickness of the shell and can reach values of up to 0.85 [4]. In contrast to the organic fluorophores that are conventionally used in biotechnology, quantum dots absorb light over a very broad spectral range. This makes it possible to optically excite quantum dots with different emission spectra (colors) by using a single excitation laser wavelength, which enables simultaneous detection of multiple markers in biosensing and assay applications. Quantum dots are made in CdSe-CdS core-shell structures that emit in the visible region from approximately 550 nm (green) to 630 nm (red). Near-infrared optical emission has been achieved with other material combinations, such as InP and InAs [5]. Currently, quantum dots with a variety of properties are available commercially.

2.2 Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) are graphitic sheets that are curled up into seamless cylinders. During the past few years they have attracted a great deal of attention, and have been subject to intense research associated with their possible application as carbon-based electronic devices. Carbon nanotubes are classified into two main types, multi-walled (MWCNTs) and single walled (SWCNTs). The earliest observations were of micron-long multi-walled nanotubes in 1991. Shortly after that, the synthesis of single walled tubes was reported [6]. Their diameters could be controllably changed via variations in the growth parameters.

2.3 Inorganic Nanotubes, Wires and Belts

Carbon nanotubes, inorganic nanotubes and nanowires are exciting increasing interest in many areas. Like carbon nanotubes, inorganic nanotubes consist of long hollow cylinders that typically have diameters of about 10 nm and wall thicknesses of about 1 nm [7]. Nanowires and nanorods are flexible

or stiff solid cylinders that are much longer than their diameters. They provide a much greater surface area for sensing applications than the area offered by spherical particles. These unusual morphologies can be synthesized from a wide variety of materials. Nanotubes have been made from semiconductor metal oxides such as ZnO and TiO₂ from sulfides, from phosphides, and other materials. Nanorods have also been formed from gold and silver. In general, the synthesis routes follow one of two paths: a gas phase synthesis in which precursors decompose at high temperature to reform as wires and rods, or a solution phase process at low temperature.

Many synthesis techniques have been reported that use the solution phase or so-called soft chemistry synthesis of nanorods, tubes and wires. Solution phase chemistry can produce many of the same materials as the gas phase route, including metal oxides as such as ZnO, indium tin oxide (ITO) and others. One of the novel methods for the synthesis of metal oxide nanotubes employs gels derived from low molecular weight organic compounds [8].

Rao [9] describe several of these methods. The so-called carbothermal route makes use of the reaction of metal oxide powders in a reducing environment with carbon nanotubes that supply a source of reactive carbon. This method produces nanowires and nanorods of metal oxides such as SiO₂, InO, ZnO, and under the right conditions of excess nitrogen, can produce nitrides of these metals and oxynitrides. One of the simple methods of synthesis of inorganic nanowires employs the carbothermal route. The method essentially involves heating a metal oxide with an adequate quantity of carbon in an appropriate atmosphere. For example, ammonia provides the atmosphere for the formation of nitrides. An inert atmosphere and a slight excess of carbon yield carbides. In these reactions, carbon helps to form an oxidic species, usually a sub oxide, in the vapor phase, which then transforms to the final crystalline product.

2.4 Gold and Silver Colloids

Nanoparticles of noble materials such as gold and silver have been used for centuries for coloring of glass and silk. The high conductivity of the noble metals supports the presence of a plasmon absorption band. This absorption band results when the incident photon frequency is in resonance with the collective excitation of the conductive electrons of the particle. This effect was termed "Localized Surface Plasmon Resonance" (LSPR). The resonant frequency of the LSPR band is strongly size dependent. Spherical gold particles of 10 to 40 nm diameter are red (resonance frequency at about 600 nm). On the other hand, irregularly shaped, and bigger particles turn blue (resonance frequency about 450 nm). The full

visible spectrum may be covered by gold particles with diameters from 60 to 200 nm. Silver nanoparticles in the same size ranges behave in a similar way. Today, colloidal gold finds application in non-linear optics, supramolecular chemistry, molecular recognition and the biosciences.[10]

2.5 Lanthanide-Based Nanoparticles

Lanthanides or rare earths metals comprise all elements bearing the atomic numbers 58 to 71 in the periodic table. Some of the lanthanide ions (e.g. Eu(III), Dy(III), Tb(III) and Sm(III)) have well determined excitation and emission spectra when they are incorporated into appropriate environments such as chelate molecules or crystal lattice of oxide. Chelates are organic complexes that serve as antennae which transmit the excitation energy to the lanthanide ion. Oxides like Gd_2O_3 or Y_2O_3 provide ideal hosts for doping with luminescent lanthanide ions [11]. The crystal lattice of the oxide permits efficient excitation and emission of the electronic transitions of their f-electrons. The lanthanide emission is narrow, exhibits a large Stokes shift, and yields long luminescence lifetimes (from several μs to ms). The use of nanoparticles containing luminescent lanthanide ions enables multiple luminescent centers to be incorporated into a single nanoparticle. Single polystyrene nanoparticle of 100 nm may contain several thousand chelate molecules, possibly with different lanthanide ions[12].

2.6 Magnetic Nanoparticles

Magnetic nanoparticles, especially magnetite (Fe_3O_4) nanoparticles, are promising candidates for biomolecule tagging, imaging, sensing, and separation. Magnetite is a common magnetic iron oxide that has a cubic inverse spinel structure with oxygen forming a face-centered cubic (FCC) structure and Fe cations occupying interstitial tetrahedral sites and octahedral sites. The electrons can hop between Fe^{2+} and Fe^{3+} ions in the octahedral sites at room temperature, thus giving the magnetite properties of half-metallic material. Using chemical precipitation methods, different nanometer-scale MFe_2O_4 materials ($M = Co, Ni, Mn, Mg, etc$) can be synthesized and used in studies of nanomagnetism[13].

For magnetic particles below a certain critical diameter, a single nanoparticle cannot support more than one domain. The critical diameter generally falls in the 10 to 100nm range given by Cheng and Chau[14]. In a single-domain cluster, the atomic magnetic moments are coupled via exchange interactions to form a large net cluster moment, the cluster is called a super-paramagnet. After surface coating and functionalization, the magnetic

nanoparticles can be dispersed into water, forming water-based suspensions. From a suspension, the particles can interact with an external magnetic field and be positioned to a specific area, facilitating magnetic resonance imaging for medical diagnosis and cancer therapy based on heating with an external AC magnetic field. These applications require that the nanoparticles are superparamagnetic with sizes of a few nanometers and a narrow size distribution so that the particles have uniform physical and chemical properties.

3. Application of Nanomaterials in Sensors

3.1 Electrochemical Biosensors Using Nanomaterials

Nanomaterials can be used in a variety of electrochemical biosensing schemes. New nanoparticle-based signal amplification and coding strategies for bio-affinity assays, along with carbon nanotube molecular wires, have been proposed during the last few years. Gold, silver and metal oxide nanoparticles have been widely used in biosensors because of their large relative surface area and good biocompatibility[15].

3.2 Bio-Sensors

A biosensor is defined as an analytical device that consists of a biological component (enzyme, antibody, receptor, DNA, cell, and so on) in intimate contact with a physical transducer that converts the biorecognition process into a measurable signal (electrical, optical, and so on) as seen in Figure. Biosensors are commonly classified as immunosensors, enzymatic (catalytic), non-enzymatic receptor, whole-cell (microbial sensors) or nucleic acid (DNA) biosensors, according to the biological recognition element. It is not necessary to incorporate a biological recognition element in a sensor device, physical adsorption onto a surface can be sufficient to change the conductivity, for example, of a thin film. The change is detected electrically and is related to the concentration of a particular analyte. Physical adsorption finds most application to gas sensors[16].

3.3 Magnetic Sensors

Magnetic or paramagnetic materials are being used as labels in a new generation of sensors. Detection of the magnetic labels can be accomplished in a variety of methods. Direct detection of magnetic materials can be achieved by a so-called Superconducting Quantum Interference Device (SQUID) developed

by Chemla.15 One of the methods for detection of magnetic particles is implemented into the Force Amplified Biosensor (FABS) developed by Baselt[16]. This biosensor measures the forces that bind DNA-DNA, antibodyantigen, or ligand-receptor pairs together, at the level of single molecules.

3.4 Gas Sensors

Semiconductor materials have found wide application as gas sensors, often referred to as electronic noses. Devices that incorporate materials such as tin oxide have been available commercially for some time. Sensors of this type operate on the principal of resistance or electrical conductivity variations as gases adsorb to the surface. Due to the selective nature of this adsorption, sensors can be developed that respond selectively to different gases in a mixture. Typically, the sensing element is made up on a thin film deposited on a substrate. Several investigators have explored the possibility of using nanocrystalline films, or layers of nanoparticles themselves, as the sensing element in the hope of achieving improved sensitivity.

A large variety of nano-scale materials have been examined for application as sensors. Metal oxides constitute a broadly applied family of materials for gas sensing. Tin oxide (SnO₂) has been widely exploited as a suitable semiconductor sensing material, commonly as nanocrystalline films, in the form of nanoparticles either by themselves or in conjunction with other nanoparticles such as functionalized copper, or as nanotubes. Tin oxide can be used to detect common air contaminants such as CO, CO₂, NO and NO₂, toxic gases such as H₂S, or ethanol in gasoline. Other nano-scale metal oxides can be used for vapor sensing. Tungsten oxide (WO₃) has been used to detect vapors of H₂S, N₂O and CO; nanostructured thin films of MoO₃ were used by Guidi [17] to detect CO and NO₂. Non-oxide materials can also be used for vapor detection. Metal nanoparticles have been used as vapor sensors by attaching long chain alkyl-thiols to the particles. The spacing of the array of nanoparticles that is formed by the chain affects the dielectric constant of the assembly and the electrical conductivity. The network of particles and polymer can accept organic vapor molecules that change the particle spacing. The nanoparticle sensors were compared with conventional thin film semiconductor devices. The nanoparticle sensor response is compared to conventional devices in Table1[18].

Table1. Comparison between the gas detection thresholds of commercial sensors and the gas detection thresholds of Nanopartical SnO₂ sensor prototypes.

Material	Electrochemical	Nanopartical Sensor
CO	5 ppm	30 ppm
NO ₂	600 ppm	500 ppm
NO	900 ppm	800 ppm
O ₃	200 ppm	200 ppm

With the exception of CO, the nanoparticle sensor was competitive with the electrochemical methods but of course can provide the ease of use that comes with a semiconductor device.

4. Conclusion

Nano-scale materials offer new functionalities for sensing. Although the application of this new class of materials in environmental sensors is in its infancy, significant advances in sensor technology can be expected to flow from the application of carbon nanotubes, inorganic nanotubes, nanoparticles and nanostructured surfaces in sensors. Devices based on these materials are expected to lead to detection devices that are sufficiently cheap and safe to be widely deployed in environmental sensor arrays.

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