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Review

Nanosensors in environmental analysis

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Abstract

Nanoscience and nanotechnology deal with the study and application of structures of matter of at least one dimension of the order of less than 100 nm (1 nm = one millionth of a millimetre). However, properties related to low dimensions are more important than size. Nanotechnology is based on the fact that some very small structures usually have new properties and behaviour that are not displayed by the bulk matter with the same composition.

This overview introduces and discusses the main concepts behind the development of nanosensors and the most relevant applications in the field of environmental analysis. We focus on the effects (many of which are related to the quantum nature) that distinguish nanosensors and give them their particular behaviour. We will review the main types of nanosensors developed to date and highlight the relationship between the property monitored and the type of nanomaterial used.

We discuss several nanostructures that are currently used in the development of nanosensors: nanoparticles, nanotubes, nanorods, embedded nanostructures, porous silicon, and self-assembled materials. In each section, we first describe the type of nanomaterial used and explain the properties related to the nanostructure. We then briefly describe the experimental set up and discuss the main advantages and quality parameters of nanosensing devices. Finally, we describe the applications, many of which are in the environmental field.

Keywords: Sensors; Environment; Carbon nanotubes; Nanotechnology

Contents

1. Introduction

Nanoscience and nanotechnology deal with the study and application of structures of matter with at least one dimension of the order of less than 100 nm (1 nm = 10^{-9} m). This is the standard way of classifying what belongs to the ‘nano’ world.

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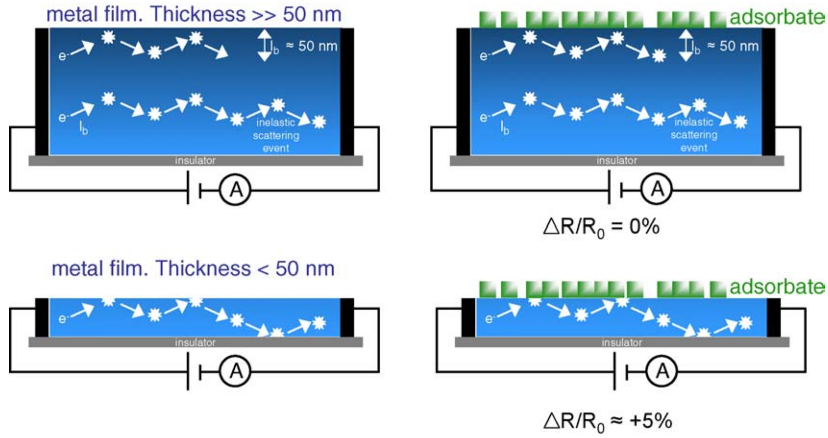

Fig. 1. Change in the measured property as a function of the thickness in resistive gas sensors. When the thickness is high (upper figure), the electrical resistance does not change because the inelastic scattering events in the bulk predominate. When the thickness of the metal film is low (lower figure), the adsorbed target molecules can be detected by measuring the change in the electrical resistance.

However, properties related to low dimensions are more important than size. Nanotechnology is based on the fact that some structures usually smaller than 100 nm have new properties and behaviour that are not exhibited by the bulk matter of the same composition.

This is because particles that are smaller than the characteristic lengths associated with the specific phenomena often display new chemistry and new physics that lead to new properties that depend on size. Perhaps one of the most intuitive effects is due to the change in the surface/volume ratio. When the size of the structure is decreased, this ratio increases considerably and the surface phenomena predominate over the chemistry and physics in the bulk. Fig. 1 shows an example of this effect (change in the measured property when the surface/volume ratio of the particle decreases) in resistive gas sensors (thin metal films).

Therefore, although the reduction in the size of the sensing part and/or the transducer in a sensor is important in order to better miniaturise the devices, nanoscience deals with new phenomena, and new sensor devices are being built that take advantage of these phenomena. New effects appear and play an important role that is often related to quantum mechanics and quantum mechanisms. Consequently, important characteristics and quality parameters of the nanosensors can be improved over the case of classically modelled systems merely reduced in size. For example, sensitivity can increase due to better conduction properties, the limits of detection can be lower, very small quantities of samples can be analysed, direct detection is possible without using labels, and some reagents can be eliminated.

Sensors have been classified according to multiple criteria [1]. The most common way to group sensors considers either the transducing mechanism (electrical, optical, mass, thermal, piezoelectric, etc.), the recognition principle (enzymatic, DNA, molecular recognition, etc.) or the applications (environmental, food, medical diagnosis, etc.). In this overview, we focus on the properties that characterise nanosensors and give them their particular behaviour. With particular focus on applications in the environmental field, we discuss the main types of nanosensors developed to date and highlight the relationship between the property monitored and the type of nanomaterial used.

In this article, we discuss several nanostructures that are currently used in the development of nanosensors, nanoelectrodes and nanodevices. In particular we focus on the main nanostructures, i.e. nanoparticles, nanotubes and nanorods. In each section we first describe the type of nanomaterial used and explain the properties related to the nanostructure. We then briefly describe the experimental set up and discuss the main advantages and quality parameters of nanosensing devices. We do not intend to provide a complete overview of the available literature, but we introduce and describe the current state of the art of nanosensors and their applications in the environmental field.

2. Sensors based on nanoparticles and nanoclusters

Nanoparticles (NPs) are clusters of a few hundred to a few thousand atoms that are only a few nanometres long. Because of their size, which is of the same order as the de Broglie wavelength associated with the valence electrons (following the wave-corpuscle duality principle, each particle can be described as a wave with wavelength λ), nanoparticles behave electronically as zero-dimensional quantum dots with discrete energy levels that can be tuned in a controlled way by synthesizing nanoparticles of different diameters. A quantum dot is a location that can contain a single electrical charge, i.e. a single electron. The presence or absence of an electron changes the properties of a quantum dot in some useful way and they can therefore be used for several purposes such as to information storage or useful transducers in sensors. Nanoparticles have outstanding size-dependent optical properties that have been used to build optical nanosensors primarily based on noble metal nanoparticles or semiconductor quantum dots.

In noble metals, nanostructures of smaller size than the de Broglie wavelength for electrons lead to an intense absorption in the visible/near-UV region that is absent in the spectrum of the bulk material. The conduction electrons are then trapped in these “metal boxes” and show a characteristic collective oscillation that leads to the surface plasmon band (SPB) observed near 530 nm for nanoparticles in the 5–20 nm range. This extinction band arises when the incident photon frequency is resonant