Nanoparticles in electrochemical sensors for environmental monitoring

Liza Rassaei, Mandana Amiri, Ciprian Mihai Cirtiu, Markus Sillanpää, Frank Marken, Mika Sillanpää

We review the state-of-the-art application of nanoparticles (NPs) in electrochemical analysis of environmental pollutants. We summarize methods for preparing NPs and modifying electrode surfaces with NPs. We describe several examples of applications in environmental electrochemical sensors and performance in terms of sensitivity and selectivity for both metal and metal-oxide NPs. We present recent trends in the beneficial use of NPs in constructing electrochemical sensors for environmental monitoring and discuss future challenges.

NPs have promising potential to increase competitiveness of electrochemical sensors in environmental monitoring, though research has focused mainly on development of methodology for fabricating new sensors, and the number of studies for optimizing the performance of sensors and the applicability to real samples is still limited.

Keywords: Air pollution; Amperometry; Electrochemical sensor; Environmental monitoring; Heavy metal; Herbicide; Modified electrode; Nanoparticle; Pesticide; Voltammetry

Liza Rassaei*
MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Mandana Amiri
Department of Chemistry, University of Mohaghegh Ardabili, Ardabil, Iran

Ciprian Mihai Cirtiu
Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal (PQ) H3A 2K6, Canada

Markus Sillanpää
Research and Innovation Laboratory, Finnish Environment Institute, P.O. Box 140, FI-00251 Helsinki, Finland

Frank Marken
Department of Chemistry, University of Bath, Bath BA2 7AY, UK

Mika Sillanpää
Laboratory of Green Chemistry, LUT Energy, Lappeenranta University of Technology, Patteristonkatu 1, 50101 Mikkeli, Finland

*Corresponding author.
E-mail: l.rassaei@utwente.nl

1. Introduction

Monitoring air, soil and water for hazardous pollutants is important and based on the need to protect the environment and public health from possible distribution of natural and industrial inorganic and organic contaminants. There is a constantly increasing need for online monitoring of contaminants in our environment, driven by new legislation and new technologies. Important examples are (i) control of wastewater quality to avoid release of synthetic drugs residues or detergents and (ii) monitoring of persistent carcinogens or residues of explosives released into the environment.

Pesticides (herbicides, fungicides and insecticides) are widely used in agriculture and industry. To limit their toxicity and their accumulation in living organisms, dose adjustment and trace-level monitoring are desirable. Thus, there is an essential need to develop new methods for simple pesticide detection at low concentrations, especially in the field.

Heavy metals occur naturally in the environment, but, due to industrialization, large amounts of heavy metals bound in fossil fuels and mineral materials have been released into the environment and deposited in trace amounts in nearly every part of the planet. Elevated levels of heavy metals in natural water may have a detrimental effect on both human health and the environment [1]. Apart from the direct impact on health or environmental problems, water or soil contamination can cause considerable economic and financial damage, so there is a need for novel instruments capable of real-time, *in-situ* detection of heavy metals and online monitoring.

Air pollution is another serious problem, especially in many heavily populated and industrialized areas, and in newly developing countries. In the majority of the developed world, legislation has already been introduced to an extent that local authorities are requested by law to conduct regular local air-quality monitoring of major urban pollutants (e.g., ozone,

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benzene, SO_2, CO, CO_2 and NO_x produced by industrial activity and transportation) [2]. In order to achieve this goal, pollutant concentrations must be monitored accurately, and ideally *in situ*, so that sources may be recognized quickly and the atmospheric dynamics of the process are understood. Growing concern worldwide about air pollution and its effect on the environment, industrial safety and hygiene has also made it essential to monitor gaseous species (e.g., SO_2, H_2S, ozone, H_2, NO_x, CO, Cl_2, NH_3, formaldehyde, ethanol, propane or ethylene oxide). Furthermore, such data would lead to real-time environmental decision-making capabilities as a result of hazardous levels being rapidly identified [2,3].

Increasing concern about the distribution and the impact of chemical reagents from analytical methodologies has led to new field methods designed to minimize use of toxic reagents during sample pretreatment and analytical measurement. Electrochemical methods for analysis can be especially sensitive, cheap and portable to provide data even in remote locations. A wide range of electrochemical sensors that fulfill the requirement to be environment friendly are commercially available. For example, sensors for water monitoring have been developed, and several of these are now advanced prototypes. Electrochemical monitoring is especially of interest for *in-situ* measurements with simple, compact and mobile equipment.

Typical electrochemical sensors comprise a sensing electrode (as transduction element), a diffusion barrier, a counter-reference electrode and an electrolyte. The analytical information is obtained from the electrical signal that results from the interaction of the target analyte and the recognition layer at the sensing electrode. Depending on the electrical signal to be measured, electrochemical techniques are divided into potentiometric, conductometric, amperometric or voltammetric methods. Different electrochemical devices have been developed for environmental monitoring, depending on the nature of the analyte, the characteristics of the sample matrix and sensitivity or selectivity requirements. The ideal sensor should possess the following characteristics [4]:

(1) specificity for the target species;
(2) sensitivity to changes in target-species concentrations;
(3) fast response time;
(4) extended lifetime of at least several months; and,
(5) small size (miniaturization) with the possibility of low-cost manufacture.

Nanoparticles (NPs) are attracting attention due to their low cost and unique size-dependent properties. The incorporation of NPs into a variety of matrices to form nanocomposite films is attracting much attention. NPs have been used in many electrochemical, electroanalytical and bioelectrochemical applications. The uniqueness of NPs is due to their mechanical, electrical, optical, catalytic and magnetic properties as well as their extremely high surface area per mass. In addition to novel properties, nanomaterials and nanotechnology open up new approaches to manufacture electrodes cost effectively by minimizing the materials needed and waste generation [5]. This is especially relevant to expensive materials (e.g., gold and platinum). For example, inexpensive materials (e.g., carbon coated by NPs) result in a large ratio of surface area to volume for low-cost sensing electrodes. In recent studies, it was demonstrated that NP electrodes could be obtained with high sensitivity and even with individual NPs giving responses [6,7].

The combination of nanotechnology with modern electrochemical techniques allows the introduction of powerful, reliable electrical devices for effective process and pollution control. Although the NPs in general play different roles in different electrochemical sensors, with regard to electroanalysis using a NP-modified electrode has several advantages:

(1) effective catalysis;
(2) fast mass transport;
(3) large effective sensor surface area; and,
(4) good control over electrode microenvironment [5].

NPs also present attractive characteristics often notably different from bulk materials in terms of both physical and chemical features. However, while several nanomaterial-based sensor systems have been reported in the literature, their implementation in routine *in-situ* devices remains a challenge. The monitoring of industrial processes with known sample matrix is usually accurate and reliable; however, *in-situ* monitoring in environmental analysis often with an unknown or changing matrix provides a bigger challenge in the development of measurement devices [8]. Electrochemical sensors have been employed for several decades for a variety of environmental monitoring applications, including monitoring of water-quality parameters (conductivity, dissolved oxygen or pH) [9], measurement of trace heavy metals [10], and carcinogens and organic pollutants (N-nitroso compounds, aromatic amines and phenols) [11]. There is a myriad of different NP materials, but they are usually divided by their chemical nature into six groups:

(1) metals;
(2) metal oxides;
(3) carbonaceous;
(4) polymeric;
(5) dendrimeric; and,
(6) composites.

Most relevant in the design of electrochemical sensors are metal and metal-oxide NPs, so these provide the focus of this review. A further topic developing from the wider use of nanotechnology (not covered in this review) is the environmental impact and potential health effects of NPs, which are still largely unknown.