Trends in Analytical Chemistry 57 (2014) 6–22

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Review

Metallic and polymeric nanowires for electrochemical sensing and biosensing

Miguel García, Pilar Batalla, Alberto Escarpa *

Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Faculty of Chemistry, University of Alcalá, Polyvalent Building E-28871 Alcalá de Henares, Madrid, Spain

ARTICLE INFO

Keywords:
Analytical performance
Biosensing
Chemical functionalization
Electrochemical microfluidics
Electrochemical sensing
Metallic nanowire
Microfluidic analytical device
Nanowire characterization
Nanowire synthesis
Polymeric nanowire

ABSTRACT

This review provides a comprehensive overview of current research involving the use of metallic and polymeric nanowires (NWs) for electrochemical sensing and biosensing. The excellent characteristics of these 1-D nanomaterials and their inherent versatility make them important building blocks for novel electrochemistry on (microfluidic) analytical devices. We outline and critically discuss synthesis, characterization, analytical performance and applications of NWs for electrochemical sensing and biosensing along with examples selected from the literature. With nanowires, we also see a horizon full of possibilities for the scientific community.

Contents

Abbreviations: MCH, 6-mercapto-1-hexanol; 1-D, 1-Dimensional; AAO, Anodic alumina oxide; AA, Ascorbic acid; CNT, Carbon nanotube; CSPE, Carbon screen-printed electrode; CVD, Chemical-vapor deposition; CE, Cholesterol esterase; COx, Cholesterol oxidase; CV, Cyclic voltammetry; DPV, Differential pulse voltammetry; ED, Electrochemical detection; EIS, Electrochemical-impedance spectroscopy; EDS, Energy-dispersive X-ray spectrometry; ESEM, Environmental scanning electron microscopy; EG, Ethylene glycol; FESEM, Field-emission scanning electron microscopy; FIA, Flow-injection analysis; GCE, Glassy-carbon electrode; GOx, Glucose oxidase; GlutOx, Glutamate oxidase; GLA, Glutaraldehyde; AuNP, Gold nanoparticle; HRP, Horseradish peroxidase; MFA, Mefenamic acid; MNW, Metallic nanowire; MB, Methylene blue; MWCNT, Multi-walled carbon nanotube; NW, Nanowire; OAP, *o*-aminophenol; PPy-COOH, Poly(1-(2-carboxyethyl)pyrrole); PVP, Poly(vinylpyrrolidone); PANI, Polyaniline; PC, Polycarbonate; PolyNW, Polymeric nanowire; PPy, Polypyrrole; PVB, Polyvinyl butyral; PAD, Pulsed amperometric detection; SEM, Scanning electron microscopy; SPE, Screen-printed electrode; SWV, Square-wave voltammetry; TBO, Toluidine blue O; TEM, Transmission electron microscopy; UA, Uric acid; XPS, X-ray photoelectron spectroscopy.

* Corresponding author. Tel.: +34 91 885 49 95; Fax: +34 91 885 49 71.
E-mail address: alberto.escarpa@uah.es (A. Escarpa).

http://dx.doi.org/10.1016/j.trac.2014.01.004
0165-9936/

1. Why nanowires for electrochemical sensing and biosensing?

Nanotechnology refers to any technology built at the nanoscale that has applications in the real world [1]. For this reason, it covers the production and the application of physical, chemical and biological systems at different scales, from individual atoms or molecules to integration of the resulting nanostructures into larger systems. Nanotechnology presents applications in many fields, so research in nanotechnology encourages breakthroughs in many different areas, such as materials, nanoelectronics, healthcare, energy or biotechnology.

For the construction of the necessary elements, two approaches are employed: top-down and bottom-up. The top-down approach is based on the modification of an original piece of material that is modeled, removing the unnecessary parts until the desired shape is achieved, like a sculptor building a statue from a raw piece of stone. It is commonly employed in electronics for construction of chips, which requires the use of a mask to protect certain parts of the material and then etched chemically (i.e. acids) or physically (i.e. UV light) to get the desired design. The bottom-up approach can be understood in the opposite way, the fabrication of nano or micro structures made by linking small pieces, as is done with bricks in building houses. Atoms and small molecules are linked to fabricate the desired object; examples of bottom-up approaches are chemical synthesis and electrochemistry, because atoms in a solution react to form a specific compound with a specific shape.

Nature inspires the design of new processes to create micro and nano devices, the bottom-up processes giving an alternative to overcome the inherent difficulties of the top-down approach, which needs complex processes and instrumentation. To start with, microsystems and nanosystems used to be usually fabricated using top-down techniques, but continual improvement in the construction of smaller devices has provided many approaches.

Mimicking nature, we can chemically control the assembly of nanomaterials as building blocks to construct new devices with innovative properties derived from nano constituents [2,3]. The discovery of new materials, shapes, processes and unexpected characteristics at the nanoscale opened up new opportunities for the development of imaginative and creative research [1,4–6].

The inherent versatility of nanomaterials produces different nano-shapes and sizes reaching the different dimensions of the material. Depending on the shape and the nanomaterial distribution, nanomaterials can be considered:

- 0-D, when they are single dots (quantum dots, fullerenes);
- 1-D, structures with only one dimension [nanotubes (NTs), nanowires (NWs), nanorods, or narrow sheets];
- 2-D, with a planar structure forming a sheet or a network (graphene); or,
- 3-D, when they possess a similar size in all dimensions but always being under 100 nm to fit the nano definition. These 3-D nanomaterials are usually formed by a combination of other nanostructures.

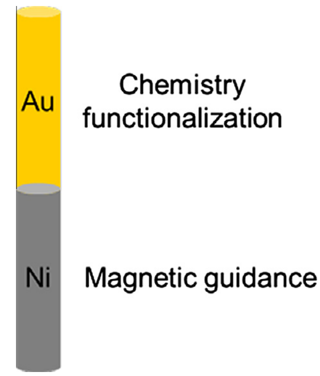

Fig. 2. Nickel-gold nanowire scheme.

Fig. 1 gives examples of each of these nanomaterials, of which NWs are 1-D and important for nanotechnology, and they can be formed from many materials. The most relevant are the metallic NWs (MNWs) and polymeric NWs (PolyNWs). MNWs are elements or oxides, and are metallic or semiconducting nanostructures with cylindrical shape, completely filled without any hollows in the structure, because, if the structure were hollow, it would be an NT. They are 1-D anisotropic structures, small in diameter and large in surface area-to-volume ratio. They can be found in different diameters from a few nm to 500 nm. The lengths of NWs are bigger, from a few μm (2–3) up to tens of μm. Because of their geometry, one of the most relevant features making them unique with respect other nanostructures is that they can be easily designed and fabricated with different segments that add controlled functionality. Fig. 2 shows an extremely simple and relevant example where a single MNW constituted by gold and nickel segments would be applied for functionalization chemistry and magnetic guidance control, respectively.

NWs capture the attention of the scientific community due to their improved functionalities compared to the bulk material. We can tailor their properties by controlling certain parameters and exploiting singular aspects of the 1-D electronic density states. As electrochemical techniques are surface dependent, the introduction of NWs opens the door to larger areas and we can expect from them improved analytical performance. In addition, the

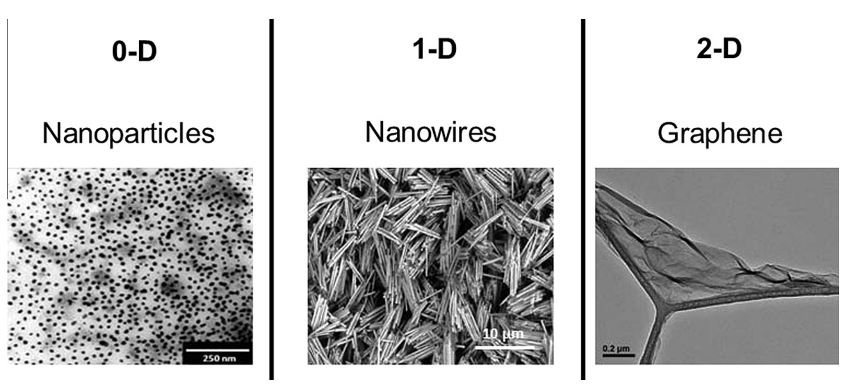

Fig. 1. Nanomaterials and their dimensional distribution.