Nanomaterials in analytical atomic spectrometry

Xiaoming Jiang, Ke Huang, Dongyan Deng, Hui Xia, Xiandeng Hou, Chengbin Zheng

Nanomaterials have attracted considerable interest in analytical chemistry (e.g., sample pre-concentration, molecular probes, and biological and electrochemical sensing). However, their physico-chemical and surface properties are significantly affected by their size and morphology, and impurities.

This article reviews the general applications of nanomaterials in analytical atomic spectrometry, including their use to improve the sensitivity and the selectivity of atomic spectrometric methods, to broaden the application range to biological-molecule detection, and to characterize and to determine nanomaterials themselves and their impurities. © 2012 Elsevier Ltd. All rights reserved.

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1. Introduction

Xiaoming Jiang, Ke Huang, Dongyan Deng, Hui Xia, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

Xiandeng Hou*

College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China Analytical & Testing Center, Sichuan University, Chengdu, Sichuan 610064, China

Chengbin Zheng*

College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

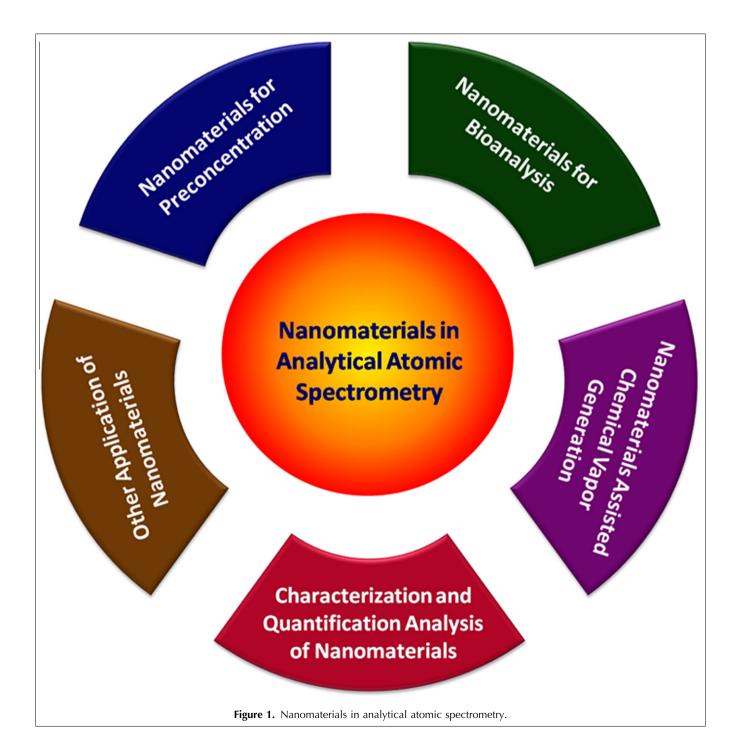
*Corresponding authors. E-mails: houxd@scu.edu.cn, abin79@163.com

Nanomaterials have nanostructured components with sizes in the range 1-100 nm in one dimension (e.g., nanolayer and graphine), two dimensions (e.g., nanowires and nanotubes) or three dimensions [e.g., nanoparticles (NPs), quantum dots (QDs) and fullerenes] [1,2]. Since surfaceto-volume ratio and quantum effects increase when the size of conventional materials is reduced down to the nano-scale, their physical and chemical properties, including thermal, mechanical, electronic, catalytical, biological and optical properties, would be significantly changed or improved [3-6], making them potentially useful for applications in sample preparation [7–10], separation [11– 13], and sensing in analytical chemistry [1,2,14–16]. There have been many reviews [1,2,5,6,12-14] that focus on different aspects of the application of various nanomaterials to analytical chemistry (e.g., sample pre-concentration, molecular probe, and biological and electrochemical sensing). However, there are no reviews focusing on the application of nanomaterials to analytical atomic spectrometry.

Analytical atomic spectrometry, including atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectrometry/mass spectrometry (ICP-AES/MS), comprises sensitive instrumental methods for determination of trace and ultratrace elements and their species in environmental, material, biological, medical, nuclear and radioactive samples [17–23]. However, matrix separation and/ or analyte-preconcentration stages are usually required to overcome matrix interference or to improve the detectability in order to achieve accurate analytical results of ultratrace elements [24-27]. Among various matrix separation and pre-concentration techniques, solid-phase extraction/microextraction (SPE/SPME) is the most common technique for routine analysis of samples with complex matrices because of its advantages of simple configuration, high recovery, fast extraction, high enrichment factor, low cost, and low consumption of organic solvents [28-30].

Due to their advantages of large surface area, chemical stability, durability, corrosion resistance, and cost effectiveness, nanomaterials have gained the greatest interest over other materials as the solid phase for SPE/SPME to improve the sensitivity of atomic spectrometry and/or minimize the interferences from complex matrices [13,31–33]. Apart from the above pre-concentration stages, a completely different approach to potential improvement of sensitivities and limits of detection (LODs), and alleviation of matrix and spectral interferences can be realized through use of chemical-vapor generation (CVG) [34–41], particularly hydride generation (HG) [37] and photochemical-vapor generation (PVG)[34–36,38–40] as sampling methods. However, the efficiency of HG or PVG is strongly affected by the chemical forms and oxidation states of analytes (i.e. the hexavalent state of selenium (Se), organic Se compounds, arsenobetaine, and arsenocholine cannot be reduced to their volatile species only by HG or PVG) [42–45].

It is well known that the electron-hole pairs (e^--h^+) would be generated and transferred to the surface of nanomaterials where they are capable of both reducing and oxidizing metal ions and organic compounds in solution, respectively, when the semiconductor nanomaterials are irradiated by UV light. Thus, nanomaterials {e.g., nano-TiO₂ [44,45] and nano-ZrO₂ [45]} combining with UV light are frequently used



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