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Titanium-dioxide nanotubes as sorbents in (micro)extraction techniques

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ABSTRACT

Titanium-dioxide nanotubes (TDNTs) are elongated nanomaterials with a large specific surface area and notable features, such as inertness, chemical and thermal stability. This overview focuses on the use of TDNTs as sorbents in sample preparation. After a brief introduction to their properties and structure, we describe the main routes of synthesis for the laboratory production of TDNTs. These routes, which comprise electrochemical, chemical-template and hydrothermal approaches, mark the ultimate application of this nanomaterial. Finally, we present the usefulness of TDNTs in solid-phase extraction (SPE), micro-SPE and solid-phase microextraction contexts on the basis of the published literature.

Contents

1. Introduction

Nanoparticles (NPs) can be defined as those particles with one or more dimensions in the nanometer range, taking 100 nm as an arbitrary limit [1], and possessing novel characteristics compared to those observed at the macroscale. Analytical chemistry, as other scientific fields, has witnessed the great impact of NPs in recent years and has taken advantage of the exceptional chemical, electric, optical, thermal and/or magnetic properties of these materials. NPs have been employed in different steps of the analytical procedure, especially sample treatment and analyte detection [2].

In sample treatment, NPs have been extensively employed to design novel extraction techniques focused on isolation and/or preconcentration of target analytes from different samples [3]. The large surface area of the NPs increases the sorptive capacity of the sorbent and also the extraction rates, as the kinetics of extraction directly depends on the contact surface between phases. The wide variety of existing NPs, covering different interaction chemistries, and their ease of synthesis and/or derivatization can be leveraged to design task-specific sorptive materials. Finally, the use of magnetic NPs, which can be easily modified in-surface, has simplified many extraction procedures.

Buzea et al. [4] proposed a classification of NPs according to different criteria, such as dimensionality, morphology, composition or uniformity and agglomeration state, as can be seen in Fig. 1. First of all, attending to the dimensionality, NPs can present one, two or

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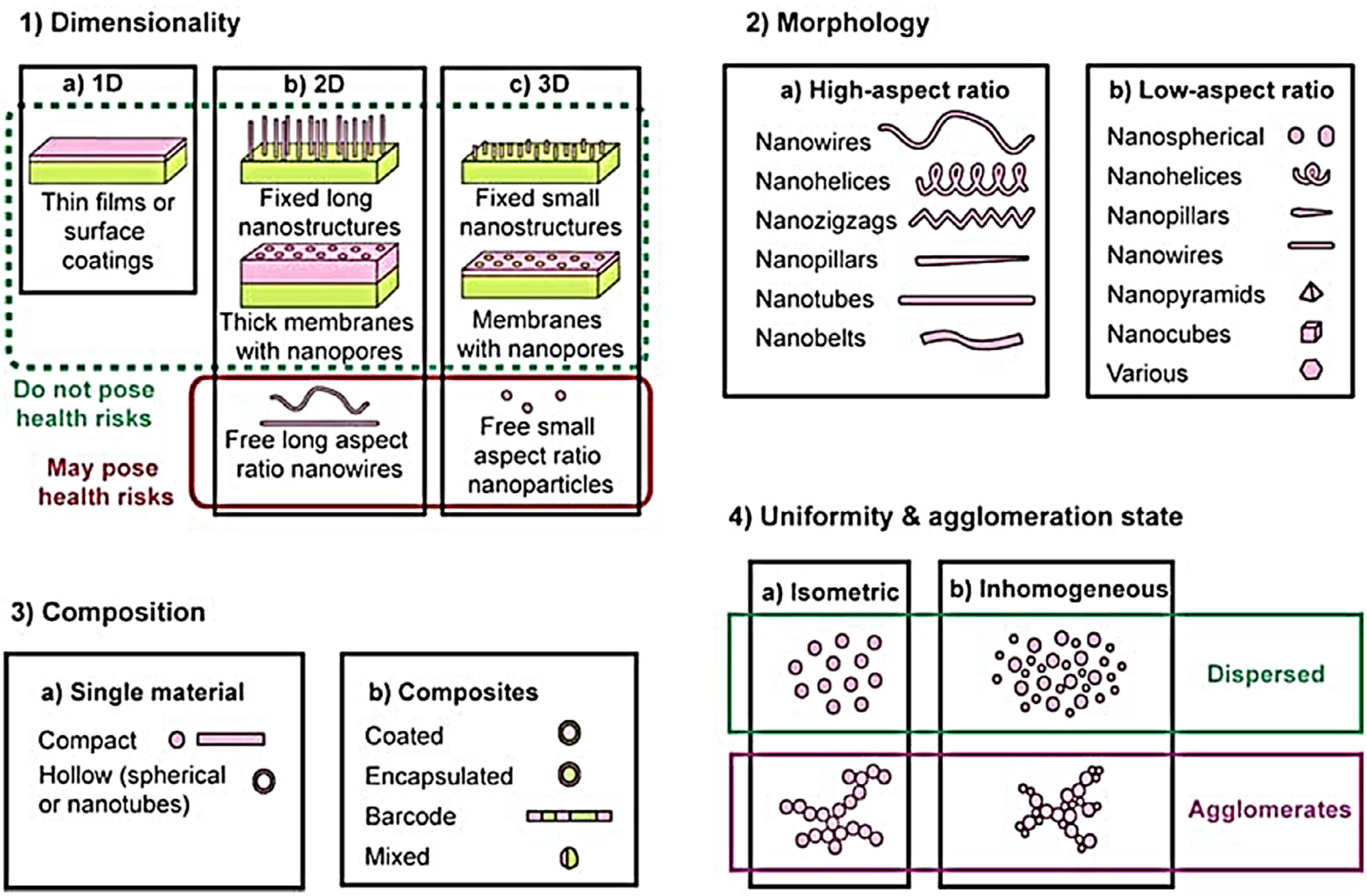

Fig. 1. Classification of NPs attending to different criteria. {Reproduced with permission of Springer from [4]}.

three main dimensions. Second, the main morphology aspects (such as flatness, sphericity, and aspect ratio) allow their classification as high-aspect or low-aspect ratio NPs. Third, NPs can be formed by a unique material or a combination of them in a synergic mode. Finally, according to their agglomeration state, they can be classified into dispersed or aggregated NPs.

An alternative, complementary classification may divide NPs in two main groups, namely organic and inorganic, according to their chemical composition. Organic NPs involve carbonaceous materials and polymeric NPs, while inorganic NPs comprise metallic and metal-oxide NPs.

Titanium dioxide (TiO_2), a metal oxide, occurs in nature in different forms, such as anatase, rutile and brookite, which differ in their crystalline structure. These minerals are used as precursors to synthesize TiO_2 at the nanoscale, where spherical particles (with sizes in the 100–200 nm range) and elongated materials are possible. Elongated materials, including nanotubes (NTs) or nanowires (NWs), present a large specific surface area and their tubular structure increases the number of potential reactive points [5]. In this sense, TiO_2-NTs (TDNTs) show notable features (inertness, chemical and thermal stability, high refractive index, non-toxicity, low cost, durability and corrosion-resistance), which have been investigated widely [6,7]. Their potential in several applications has received great attention {e.g., environmental purification and decomposition of organic pollutants, photocatalysts and self-cleaning coatings, photoelectrochemical hydrogen generation, hydrogen storage, gas sensing, biomedical applications and electrode materials for dye-sensitizing solar batteries [8–13]}.

The structure of TDNTs is not exactly defined, although several studies show that the crystalline structure of TDNTs is hydrogen titanate, where TiO_2 sheets are rolled and separated by H^+ ions [14]. TDNTs exhibit multi-walled, scroll-type, open-ended structures with large internal and external surfaces, as well as interlayer spaces. These peculiar microstructures render TDNTs favorable for applications as sorbents.

According to the previous classification, TDNTs are 2D single materials with a high-aspect ratio, easily dispersed in aqueous media. Their homogenous dispersion depends on the conditions of synthesis and the subsequent chemical treatment.

Fig. 2 shows the situation of TDNTs with respect to other elongated structures [15].

2. Synthesis of titanium-dioxide nanotubes

TDNTs can be synthesized following three different and well defined routes, namely: electrochemical approach; chemical-template synthesis; and, alkaline hydrothermal treatment [16]. We briefly describe these routes of synthesis in the following subsections.

2.1. Electrochemical approach

TDNT arrays can be prepared by anodic oxidation using titanium foil or fibers as precursors. The synthesis is usually developed at room temperature in an electrochemical reactor where titanium foil acts as anode and platinum foil as cathode. The reaction