



Carbon coated titanium dioxide nanotubes: Synthesis, characterization and potential application as sorbents in dispersive micro solid phase extraction



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ABSTRACT

In this article, carbon coated titanium dioxide nanotubes (c-TNTs) have been synthesized. The synthesis of the bare TNTs (b-TNTs) using anatase as precursor and their coating with a caramel layer have been performed by simple and cheap hydrothermal processes. The final conversion of the caramel layer in a carbon coating has been accomplished by a thermal treatment (600 °C) in an inert (Ar) atmosphere. The c-TNTs have been characterized by different techniques including transmission microscopy, infrared spectroscopy, X-ray powder diffraction, thermogravimetry and Brunauer, Emmett and Teller (BET) adsorption isotherms. The extraction performance of the c-TNTs under a microextraction format has been evaluated and compared with that provided by b-TNTs and multiwalled carbon nanotubes (MWCNTs) using naproxen and ketoprofen as model analytes. c-TNTs provided better results than the other nanoparticles, especially at low acidic pH values. In addition, c-TNTs presented a better dispersibility than MWCNTs, which is very interesting for their use in dispersive micro-solid phase extraction. Finally, a microextraction format, adapted to low sample volumes, has been proposed and applied for the determination of naproxen and ketoprofen in saliva and urine samples by liquid chromatography with UV detection. The results indicate that this approach is promising for the analysis of biological samples. In fact, the recoveries were in the range between 96% and 119% while the precision, expressed as relative standard deviation, was better than 8.5% and 26.3% for urine and saliva, respectively. The detection limits were in the range 34.1–40.8 µg/L for saliva samples and 81.1–110 µg/L for urine samples.

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1. Introduction

Titanium dioxide naturally exists in different forms such as anatase, rutile and brookite that differ in their crystalline structure. These minerals are used as precursors to synthesize TiO₂-structures at the nanoscale level where spherical particles and elongated materials are possible. Elongated materials, including nanotubes or nanowires, present a large specific surface area and their tubular structure increases the number of potential reactive points [1]. In this sense, titanium dioxide nanotubes (TNTs) exhibit remarkable features (inertness, chemical and thermal stability, high refractive index, non-toxicity, low cost, durability and corrosion-resistance), which have been widely investigated in the last few decades [2]. Their potential in several applications such as 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, have received great attention [3].

TNTs structure is not exactly defined, although several studies show that crystalline structure of titanium dioxide nanotubes is hydrogen titanate where TiO₂ sheets are rolled and separated by H⁺ ions [4]. TNTs exhibit multi-walled scroll type open-ended structures with large internal and external surfaces as well as interlayer spaces. TNTs can be synthesized following three different and well defined routes, namely: electrochemical approaches [5], chemical template synthesis [6] and alkaline hydrothermal treatment [7].

The hydrothermal method has been extensively used in the last few years due to its simplicity. In this method, an alkaline treatment at high temperature produces the delamination of anatase titanium dioxide nanoparticles (precursors) yielding single-layer Na⁺ intercalated titanium dioxide sheets. The titanium dioxide sheet

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structure is a high energetic system, being unstable due to its high surface-to-volume ratio. To reduce the surface energy, the layered nanosheets curl, resulting in the formation of nanotubes. After their synthesis, the titanium dioxide nanotubes are treated with acid in order to substitute the remaining sodium ions [8].

Titanium dioxide nanotubes obtained after alkaline hydrothermal synthesis exhibit a high specific surface area, specific pore volumes and ion-exchange capacity [7,9]. Bare titanium dioxide nanotubes (b-TNTs) have been used in solid phase extraction (SPE) to isolate and preconcentrate compounds with a wide range of polarities from water samples. Among them, benzoylurea insecticides [10], organophosphorous pesticides (chlorpyrifos, phorate and methyl parathion) [11], polycyclic aromatic hydrocarbons (PAHs) [12], dichlorodiphenyltrichloroethane (DDT) and related metabolites [13], can be highlighted.

b-TNTs have also been used as an extracting phase in solid phase microextraction (SPME). In this case, b-TNTs are formed on a fibre surface using the electrochemical synthetic approach. This synthesis produces a nanotube array which has been used for the extraction of PAHs [14], pyrethroid insecticides [15], and some fungicides (as thiram, metalaxyl, diethofencarb, myclobutanil and tebuconazole) [16], polychlorinated biphenyls [17] and organochlorine pesticides [18] at trace level from water samples. In most of the cases, the analytes are thermally desorbed from the fibre and further analyzed by gas chromatography.

Although TNTs surface provides high efficiency for the extraction of different compounds, it can be also modified to improve the selectivity or the extraction capacity. In this sense, TNTs have been functionalized with octadecyl groups to achieve the extraction of PAHs from water samples [19]. Their potential surface charge, which depends on the working pH, has been used to form hemimicelles of cetyltrimethylammonium bromide [20] to solve a similar analytical problem.

The combination of TNTs with other nanoparticles, producing the so-called hybrid nanomaterials, has also been proposed. Their combination with Au nanoparticles and n-octadecanethiol to determine PAHs in water samples [21] and the use of Zr doped TNTs for the enrichment of bisphenol A from water samples [22] are examples of this trend.

In this article, the synthesis, characterization and potential uses of carbon coated TNTs (c-TNTs) in sample preparation are proposed for the first time. For this purpose, the determination of two non-steroidal anti-inflammatory drugs in saliva samples was selected as model analytical problem.

2. Experimental

2.1. Reagents

All the reagents were of analytical grade or better. The analytes, naproxen and ketoprofen, were purchased from Sigma–Aldrich (Madrid, Spain). Stock standard solutions of each analyte were prepared in methanol at a concentration of 1 g/L and stored at 4 °C in the dark. Working standards were prepared daily by dilution of the stock solutions in ultrapure water (Millipore Corp., Madrid, Spain), the pH being adjusted to the appropriate value.

Acetonitrile, acetic acid (both from Panreac, Barcelona, Spain), and ultrapure water were employed as components of the chromatographic mobile phase.

Titanium dioxide anatase (nanopowder, <25 nm particle size, 99.7% trace metals basis) was used as the precursor of titanium dioxide nanotubes. The synthesis required the use of sodium hydroxide, sodium dodecyl sulphate (SDS), hydrochloric acid and glucose. All these reagents were purchased from Sigma–Aldrich.

For comparative purposes, MWCNTs (from Sigma–Aldrich) were used. MWCNTs present purity higher than 95%, diameter in the range of 6–9 nm and average length of 5 μm.

2.2. Sample collection and storage

Blank saliva samples were collected from healthy volunteers, using a citric acid solution as stimulus. Food and liquids (apart from water) ingestion, chewing gum and tooth brushing were avoided 30 min before sampling. The whole saliva (2.5–3 mL approximately) was spitting into a polypropylene commercial sterile pot (Deltalab, Barcelona, Spain) and stored at 4 °C until the final analysis (performed in the same day of the collection). Before its extraction, the sample was adjusted to pH 1.5 with hydrochloric acid and centrifuged at 3800 rpm for 8 min to remove denatured proteins.

Blank urine samples from healthy individuals were collected and stored in PTFE flasks at 4 °C until the final analysis (performed in the same day of the collection). Before its extraction, the sample was diluted 1/1 (v/v) with water and adjusted to pH 1.5 with diluted hydrochloric acid.

2.3. Synthesis of titanium dioxide nanotubes

Three different TNTs were synthesized, namely: bare titanium dioxide nanotubes (b-TNTs); sugar coated TNTs (s-TNTs) and carbon coated TNTs (c-TNTs).

b-TNTs were synthesized as follows: 0.5 g of SDS was mixed with 50 mL of a 10 M NaOH solution and filtered to remove the excess of SDS. Afterwards, 1 g of anatase was added and dispersed in the alkaline solution. The dispersion was sonicated for 30 min and further heated at 130 °C for 24 h. During the first 6 h, the dispersion was mechanically stirred every 30 min. After 24 h, the dispersion was vacuum filtered through a 0.45 μm PTFE membrane. The material was washed with water and 1 M HCl until the eluate became acid (ca. pH 2). The product was finally dried in an oven at 80 °C for 6 h.

s-TNTs were synthesized starting from b-TNTs. For this purpose, 250 mg of b-TNTs were mixed with 50 mL of a 0.5 M glucose solution and sonicated in an ultrasonic bath for 45 min. Then, the mixture was heated at 160 °C for 5 h producing a brown dispersion. The material was washed with water to remove the glucose excess, leaving TNTs covered with a layer of caramel. The solid was dried in an oven at 80 °C for 6 h.

c-TNTs were obtained using s-TNTs as precursors. 200 mg of s-TNTs were introduced in a hermetic copper tube which was purged with Ar in order to remove residual oxygen. The tube was heated at 600 °C for 3 h yielding a black powder.

2.4. Titanium dioxide nanotubes characterization

Transmission electron microscopy (TEM) images were recorded by use of a JEOL JEM 1400 microscope (Isaza, Alcobendas, Spain) operating at an accelerating voltage of 120 kV. The TEM micrographs were used to characterize the nanoparticles size and morphology. Micrographs were acquired in the Central Service for Research Support (SCAI) of the University of Córdoba. Infrared measurements were performed in a Bruker Tensor37 FT-IR spectrometer, equipped with a diamond attenuated total reflectance (ATR) cell with a circular surface of 3 mm diameter and three internal reflections. A Deuterated Triglycine Sulfate (DTGS) detector was used for spectra acquisition. Spectra were collected between 4000 and 500 cm⁻¹ at a 4 cm⁻¹ resolution with 64 coadded scans each. Data collection was made using OPUS software (Bruker, Ettlingen, Germany).

The thermogravimetric analysis (TGA) curves were registered using a TGA/DSC 1 Star System (Mettler Toledo). Samples were

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