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A new approach to the synthesis of titania nano-powders enriched with very high contents of carbon nanotubes by electro-spinning

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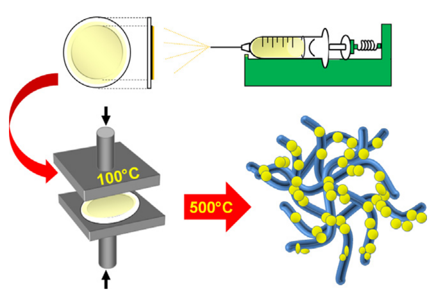
HIGHLIGHTS

- A new approach to synthesise oxide nanopowders enriched with CNTs is proposed.
- The method, based on the electro-spinning technique, is shown in the case of titania.
- TiO_2 nanopowders with 38–88 wt% CNTs and good interfacial interaction are produced.
- Influence of polymer and TiO_2 precursor on the powders properties is investigated.
- The solution viscosity controls morphology and crystalline phase of the nanopowders.

GRAPHICAL ABSTRACT



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ABSTRACT

A new and very simple approach to the synthesis of oxide nanopowders enriched with very high contents of carbon nanotubes (CNTs) is proposed. The procedure consists of three steps: 1) generation of nanofibres over mats of CNTs via the electro-spinning technique; 2) thermo-mechanical treatment of the so-prepared composite to improve interfacial interaction between as-spun fibres and carbonaceous support; 3) calcination in air to obtain the desired oxide from its precursor. Its ease and efficacy are here demonstrated in the case of titania, but the proposed procedure can be extensively used for any other oxide, provided that it can be prepared by ES technique. In this preliminary study, a fixed titanium concentration (0.9wt%) in the solution to be spun is considered, and the influence of titania precursor (titanium butoxide or titanium isopropoxide) and type of polymer (polyvinilpyrrolidone or polyvinilacetate) on morphology and crystalline phase of the oxide nanoparticles is investigated. Viscosity of the precursor/polymer solution is found to chiefly control not only morphology of the oxide, but indirectly also its crystalline phase. CNT load of the hybrids ranges between 38 and 88 wt%.

1. Introduction

CNT-based composites have attracted much attention due to

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their unique properties and promising applications [1–3]. Different methods (including capillary action, supercritical fluid deposition, chemical vapour deposition) have been used to coat or decorate CNTs with metal oxides, precious metal nanoparticles, polymers and functional organic molecules [4–10]. These composites are endowed with electronic, mechanical, adsorption and thermal properties typical of CNTs and, in addition, exhibit cooperative or synergetic effects. Titanium dioxide (TiO_2) has been used as a building block to develop new nano-architectures with advanced properties and, hence, improved performances in the field of sensing [11–13], photo-catalysis [14,15], and photovoltaic [16,17]. In particular, the pairing of titania with CNTs allows designing hybrid materials with various potential applications. The production of TiO_2-CNTs and, more generally, of hybrid materials is generally accomplished through conventional techniques, such as sol–gel. In the last decade, electro-spinning (ES) has gathered remarkable attention among the manifold synthesis methods. This technique allows obtaining one-dimensional nanostructures in the form of fibres, wires, rods, belts and tubes [18–20] and provides numerous advantages with respect to conventional methods. It is a simple, inexpensive and scalable methodology that allows continuous preparation of fibres with nanometre and micrometre diameters and with high surface area/volume ratio [20,21].

The typical ES apparatus consists of a syringe, a grounded collector and a high voltage power supply. In the spinning process, the syringe is filled with a polymer solution and a high voltage is applied between the syringe nozzle and the collector. The interaction between the charged polymer solution and the applied electric field provides the extrusion force. Almost any soluble polymer can be electro-spun if its molecular weight is high enough. Nonetheless, many parameters (operating conditions: applied voltage, solution feed rate, spinning distance…; environmental conditions: temperature, humidity…; solution properties: conductivity, viscosity, surface tension…) have to be carefully adjusted in order to control morphology and properties of the electro-spun materials [18,19,22].

Several studies have focused on obtaining TiO_2-CNTs composites by electro-spinning [23–26]. These composites have been used in dye-sensitised solar cells [27] and as electrodes in ion–lithium batteries [28]. In the first case, ES gave uniformly distributed, highly porous, crystalline rice grain-shaped TiO_2 nanostructures, endowed with better photo-catalytic performances with respect to the same material obtained through other techniques. In the second case, ES led to the fabrication of one-dimensional nanostructures with enhanced electronic conductivity with respect to the pristine TiO_2, i.e. of a hybrid material with appealing properties for anode applications. However, it is known [21] that viscosity of the solution to be spun plays a key-role: it determines the range of concentrations within which continuous nanofibres (NFs) can be obtained. Of course, the addition of CNTs to the solution affects its viscosity. Unfortunately, small relative amounts of CNTs are able to make it unsuitable for electro-spinning. Moreover, our work has recently demonstrated that the presence of CNTs within the just-formed TiO_2 structures could destabilise them [29]. Indeed, some research groups [23,24] prepared hybrid NFs and mats of CNTs/TiO_2 nanoparticles (NPs) with enhanced mass ratio (100:20) by combining sol–gel and ES techniques.

In this work, a new three-step procedure to synthesise titania nanopowders enriched with very high CNTs contents is proposed in order to overcome this limiting aspect (Fig. 1). The procedure basically consists in 1) generation, via ES, of nanofibres over CNT mats prepared by filtration, 2) thermo-mechanical treatment of the so-prepared composite for adhesion purposes (Fig. 2), and 3) final calcination in air. It can be extensively used to prepare CNT-enriched nanopowders of *any other* oxide, provided that the oxide can be prepared by ES technique. The influence of precursor and type of polymer on morphology and crystalline phase of the oxide NPs is preliminarily investigated for a given (0.9 wt%) titanium concentration in the precursor/polymer solution, selecting titanium butoxide (TBT) or titanium isopropoxide (TIP) as precursors, together with polyvinilpyrrolidone (PVP) or polyvinilacetate (PVAc) as polymers. A combination of analytical techniques including scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray photo-emission spectroscopy (XPS) and micro-Raman spectroscopy (MRS) is utilised for the characterisation of the materials synthesised at each step of their preparation.

2. Materials and methods

2.1. Preparation of the samples

Commercial CNTs (Helix Materials; nominal outer diameter: 10–30 nm; nominal length: 0.5–40 μm; purity >95%) were used to prepare mats to be used as supports. As received CNTs were functionalized as reported in a previous work [30]. Briefly, nanotubes (0.5 g) were dispersed in 100 ml of concentrated HNO_3 (65%) at

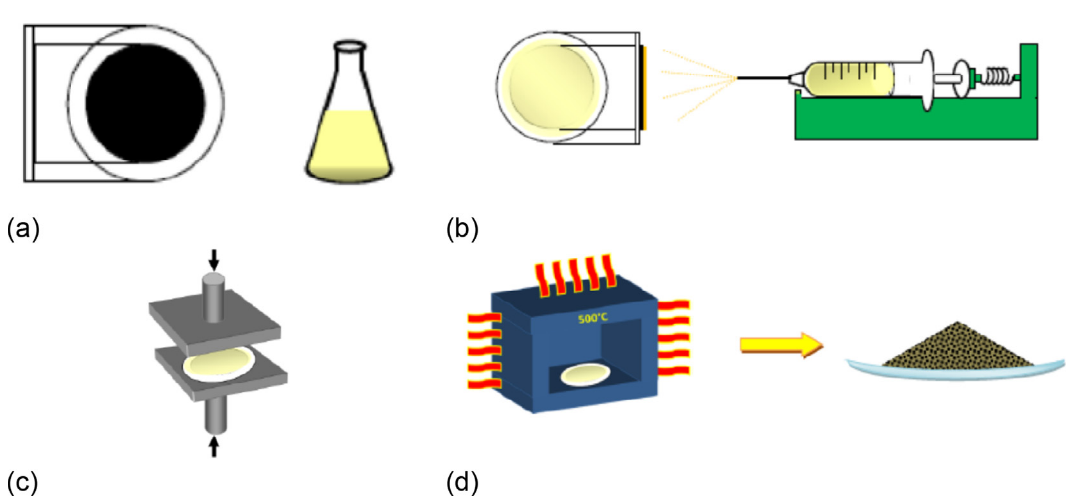

Fig. 1. Main steps of the method proposed to synthesise oxide-nanopowders enriched with very high CNT contents: (a) preparation of CNT-based support and spinnable solsolution; (b) deposition of NFs over CNT mats by ES; (c) thermo-mechanical treatment and (d) calcination of the as-prepared nanocomposites.