

Solid State and Template Free Synthesis of a Nanotubular Polyaniline-TiO₂ Composite

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ABSTRACT

Hybrid organic-inorganic nanomaterials are the focus of much attention due to their capacity to enhance electronic and conductance properties of both materials. One important feature is the nanostructuring of such composite. We report herein on the synthesis of a polyaniline-Titania TiO₂ composite. The chemical characteristics of the composite are discussed and compared to polyaniline and TiO₂ characteristics. Innovative was the nanostructuring of the composite in a tubular form and the polymerisation of aniline inside the Titania nanotubes. The as made nanocomposite showed a better dispersibility than the Titania nanotubes.

Keywords: polyaniline, titanium dioxide, nanomaterial, nanotubes, composite

1 INTRODUCTION

Conductive polymers have numbers of application potentials mainly in chemical and biological sensors development [1]. This is one of the main reasons for the intensive investigations and studies conducted on these materials. Electronic properties of these materials can be modified and adapted to different applications by modifying their structure during the synthesis. Amongst conductive π -conjugated polymers, polyaniline (PAni) has a high conductivity and can easily be produced via a chemical or an electrochemical route. A further increase in conductivity of the PAni would lead to a very promising material in various applications and to enhancement of sensors performances. This can be reached using metal oxides to produce hybrid organic-inorganic composites with a high conductivity. Such composites have attracted much interest since they permit to combine both electronic and optical properties for applications such as optoelectronic devices or sensors [2], using either conducting polymers or carbon nanotubes [3]. It was shown that hybrid organic-inorganic materials permitted a significant enhancement of conductance properties of both materials [4]. Amongst all metal oxides titanium dioxide (TiO₂) has gained strong interest as it exhibits both a high chemical stability and photocatalytic properties to degrade organic pollutants [5]. Mo et al. [6] studied the variations of polyaniline conductivity produced by the polymerisation of aniline on titanium dioxide nanoparticles. They have demonstrated that the composite PAni-TiO₂ synthesized

showed an enhancement in conductivity attributed to a better charge transport network. These hybrid materials also show promising features specially for sensing applications. Up to now most studies in this field reported on the synthesis of micron-sized rods or nanoparticulate composites of PAni and rutile- or anatase-TiO₂ [6-13]. In most studies the authors observed that not only physical and chemical properties are improved in the composites but also the presence of polyaniline improves the dispersibility of the nanoparticles compared to TiO₂ nanoparticles that are aggregated in solution. Bian et al. [10] suggested that polyaniline permitted to stabilize the titanium nanoparticles in solutions. Xiong et al. [14] reported on the synthesis of hybrid microwires of PAni-TiO₂ with a uniform arrangement. Their synthesis involved the use of an anodic aluminium oxide membrane template with microchannels where polymerisation of aniline took place. The microwires presented a rough surface and were larger in diameter than the channels of the template.

We report herein on the synthesis of a nanotubular composite of PAni and titania-TiO₂ via an easy mechanochemical route and avoiding any template use. Interest relies on the possibility of both a larger surface available for adsorption and reactivity and providing channels for enhanced electron transfer to improve conductivity. Thus such hybrid tubular unfilled material could have a strong interest in studying confinement effect of molecules.

2 EXPERIMENTAL

2.1 Materials and instruments

Aniline hydrochloride and Iron (III) chloride hexahydrate were purchased from Aldrich and used as received. Titania nanotubes were synthesized and furnished by Elcass Laboratory in Strasbourg and were used as received. Toluene (analytical reagent) was purchased from Fisher Scientific. Polyaniline nanofibers used as a reference material were synthesized on our own via a chemical oxidative route [15]. Scanning Electron Microscopy (SEM) images were obtained on a Zeiss DSM 982 Gemini[®] in field emission mode and Transmission Electron Microscopy (TEM) images were obtained on a Topcon 002B[®] equipped with an EDX Noran[®] for elemental analysis. Fourier Transform Infra-Red (FTIR) spectra were recorded on a Bruker Tensor 27[®] instrument between 400 and 4000 cm⁻¹. Wide angle X-

ray diffraction (XRD) spectra were performed on a Bruker Advance D8[®] instrument with a SolX detector in the range $2\theta=5^\circ$ to 80° . Thermogravimetric analysis were performed under air flow with a Seiko Exstar 6000 Instrument[®].

2.2 Synthesis of TiO₂ Nanotubes

Titania nanotubes were synthesized by the hydrothermal treatment of TiO₂ powder in 10M concentrated NaOH solution at 130°C [16]. In a typical synthesis, 1g TiO₂ (P25, Degussa) powder was added to 50mL of solution in a Teflon autoclave, stirred for 1h, and digested at 130°C for 24h. After the hydrothermal treatment, the white powder obtained was vacuum filtered and washed with 2M HCl and distilled water until neutral pH, followed by overnight drying at 110°C. After drying overnight, the powder was dried and calcined for 2h at 380°C.

2.3 Synthesis of PANi-TiO₂ nanocomposite

The synthesis process was based on a method described by Du et al. [7] to produce polyaniline nanofibers. The nanocomposite was produced via a mechanochemical route. First 100 mg of titania nanotubes were ground with 520 mg of aniline hydrochloride salt in a large agate mortar in order to soak and fill in the titania nanotubes with the aniline monomer precursor. Then 2,16 g of Iron(III) Chloride salt was added to the mixture to act as the oxidant in the chemical oxidative polymerisation process of aniline. After about 8 minutes thoroughly grinding the mixture it changed from powder to slurry. Grinding of the slurry continued until it turned from an orange coloured mixture to a green coloured sludge indicating the formation of polyaniline accompanied by the reduction of the Fe³⁺ ions. The product was then filtered and rinsed on a funnel buchner with deionized water and dried at 60°C under dynamic vacuum. The residual product was stored in a closed pill and in a dry place before further characterization. The nanocomposite was used as made for each characterizations techniques except for TEM analysis, which were performed after diluting a small fraction of the product in ethanol, and for FTIR analysis performed on KBr pellets with a product content of 0,5% in mass.

3 RESULTS

TEM and SEM images (figure 1) show a dense fiber/tubes mat composed of nanotubes of 15nm in diameter and 100nm to 200nm nanometer long. Therefore the composite nanotubes are better dispersed than the initial TiO₂ nanotubes (figure 1c,d). Titania nanotubes are single thin wall nanotubes. On the TEM image of the composite (figure 1c) two types of short nanotubes are observed, single wall nanotubes and thickened wall nanotubes. This phenomenon was ascribed to the polymerisation of aniline at the internal surface of the TiO₂ nanotube. Longer nanotubes/ nanofibers are observed in fractal zones as seen

in the framed zone on figure 1b. These are smaller in diameter than the tubules. As TiO₂ nanotubes are shorter than these nanotubes/nanofibers, we assumed these long nanofiber/nanotubes were pure polyaniline uncovered by TiO₂ nanotubes. Synthesis of polyaniline nanofibers is then supposed to occur inside the TiO₂ nanotubes together with coating of polyaniline on the internal surface of nanotubes walls.

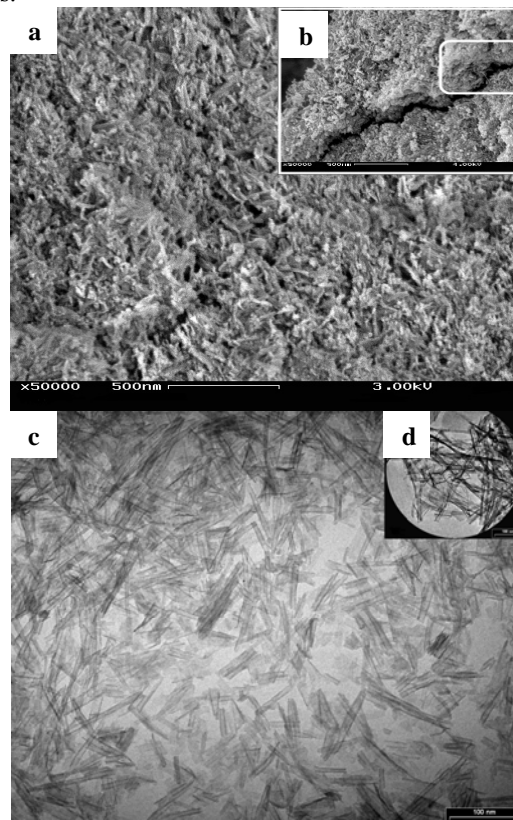


Figure 1: SEM (a, b) and TEM (c) images of the nanocomposite and TEM image (d) of TiO₂ nanotubes.

Assumption that the polymerisation occurred inside the titania nanotubes was verified by testing affinity of the different materials involved in the synthesis to either water as an aqueous phase or toluen as an organic solvent. Pure polyaniline nanofibers, dried TiO₂ nanotubes and the as synthesized composite were dispersed in toluen in three different flasks and sonicated for 2 minutes to ensure a good dispersibility of the material in the solvent. Deionized water was then added to each medium with a ratio toluen: water of 1:1. After ten minutes undisturbed, the titania nanotubes have left the organic phase for the aqueous one. The polyaniline gathered in the toluen phase just over the interface between toluen on top and water at the bottom. The nanocomposite material avoided the toluen phase and stucked to the glass wall of the flask. A fraction of the composite has left the organic phase for the aqueous one. These observations confirmed the assumption that polyaniline was mainly synthesized inside the TiO₂ nanotubes and only a small part of polyaniline could be in

contact with toluen. This is in accordance with the presence of a fraction of the synthesized nanocomposite at the external surface of the toluen phase.

During TEM observations of the nanocomposite we performed elemental analysis of the composite (figure 2). It showed a sharp peak at 4,519eV followed by a second peak less intense at 4,941eV which are characteristic of the presence of Ti in the composite material. Thus a less intense but significant large organic peak can be clearly identified at an energy level of 0,53eV. This peak can be attributed to the contribution of oxygen, carbon and nitrogen. These results prove that we have synthesized an organic-inorganic material.

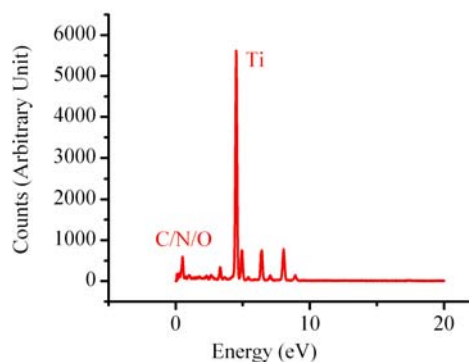


Figure 2: EDX analysis of the nanocomposite.

We can also assume that the as synthesized material is a composite of an organic phase that is supposed to be polyaniline and an inorganic phase composed of titanium oxide. This result was confirmed by the FTIR spectrum of the nanocomposite (figure 3a) showing characteristic bands of polyaniline [17] at 3223cm^{-1} and between 1611cm^{-1} and 1152cm^{-1} .

The TiO_2 spectrum (figure 3b) shows two vibronic bands at 3346cm^{-1} and 1634cm^{-1} which are attributed to the hydroxyl groups on the surface of TiO_2 .

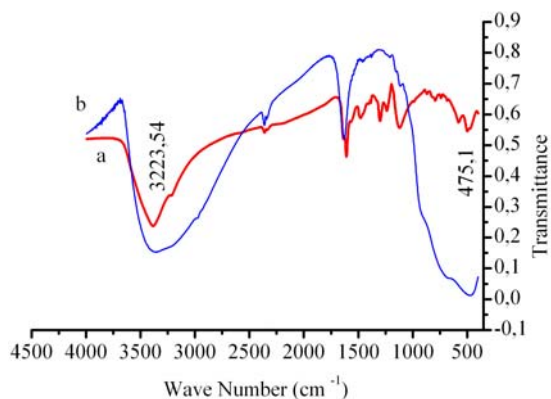


Figure 3: FTIR spectra of (a) PAni- TiO_2 nanocomposite and (b) TiO_2 nanotubes.

The broad peak at 475cm^{-1} is attributed to the characteristic strong absorbance of TiO_2 due to an O-Ti-O network [18].

The intensity of this band is reduced in the composite spectrum suggesting interactions between polyaniline and its inorganic counterpart of TiO_2 via H-bonding.

XRD spectrum of the composite material confirmed the FTIR spectra. It showed both characteristic crystallin peaks of Titania- TiO_2 and contribution from the polyaniline. This revealed that the polyaniline fraction of the composite has some degree of crystallinity [10,19]. Thermal analysis was performed to measure the relative contributions in mass of each organic and inorganic parts in the solid. A second objective was to further characterize the potential interactions between these two parts in the nanostructured composite. The material was heated from 25°C to 600°C with a heating rate of 5K per minute and under air flow. Doped polyaniline was assumed to decompose between 250°C and 400°C . The decomposition of polyaniline in its emeraldine salt form involved three distinct stages of weight loss, confirmed by the literature [7]. First stage occurred at a temperature around 100°C and was mainly caused by the removal of free water. The second stage at about 250°C was attributed to the loss of dopants (HCl). The third stage occurred between 400°C and 500°C and was caused by the thermal decomposition of the polymer chains. Pure polyaniline material was totally degraded by the thermal treatment up to 600°C .

The differential thermal analysis (figure 4b) of the composite shows a sharp peak which was attributed to the loss of free water. A large peak occurs between 250°C and 450°C . We assumed that this peak was composed of multiple merged peaks which could be attributed to the loss of dopants and to the degradation of both the composite and the polymer chains. The thermal gravimetric analysis (figure 4a) shows a first weight loss (18%) due to the loss of free water and a second weight loss of about 37% accompanying the degradation stages of polyaniline in its acid doped form. Thus the FTIR spectrum of the residual product after heating the composite up to 600°C showed only characteristic bands of TiO_2 . This confirms our assumption that this large peak was due only to polyaniline decomposition. Then we supposed that there was a third peak confused between the second stage and the third stage of polyaniline decomposition. That peak was ascribed to the breaking of H-bonding between polyaniline chains and the inorganic TiO_2 . This phenomenon was assumed to occur just after the loss of dopants and before the decomposition of polyaniline chains. The different stages were supposed to occur at temperatures so closed to each other that it didn't permit us to separate the three contributions at a macroscopic scale. Therefore degradation temperature of the composite was a little weaker than that observed for pure polyaniline. Interactions between polyaniline and TiO_2 were supposed to weak the interactions of inter-chains in polyaniline conducting to the degradation of the skeleton of polyaniline chains at a lower temperature [10].

The inserted graphic at the top right of figure 4 shows thermogravimetric measurements of the TiO_2 and confirms that the thermogravimetric results obtained were due to the

polyaniline and interactions between the polymer and the TiO₂.

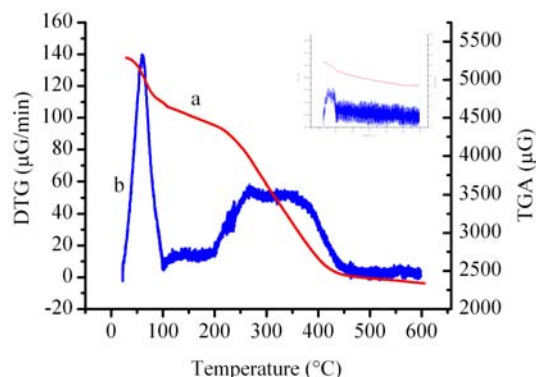


Figure 4: Thermogravimetric analysis (a, b) of the composite and (c, d inserted graphic) of the TiO₂ nanotubes

The as made nanocomposite was composed of 45% TiO₂, 37% doped polyaniline and 18% free water, suggesting that not all aniline reacted with the oxidant to polymerise.

4 DISCUSSION

We have demonstrated that a self assembled composite nanomaterial of polyaniline and titania can easily be produced via a mechanochemical route. In a typical process aniline hydrochloride, titania nanotubes and Iron(III) chloride were mixed together. Grinding of the mixture causes the polymerisation of aniline on titania and the formation of composite nanotubes accompanied by the reduction of Fe³⁺ acting as the oxidant in the polymerisation reaction.

The as synthesized product is a nanostructured composite of aniline and TiO₂ with a ratio of 45:55 in mass. Morphological observations of the composite at the nanoscale showed a dense mat of short nanotubes, which were assumed to be composed of both polyaniline and TiO₂, and longer nanofibers/nanotubes smaller in diameter than the nanotubes which were supposed to be pure polyaniline uncovered by titania nanotubes. The nanotubular composite showed a hydrophilic nature and avoided toluene suggesting that the polymerisation occurred inside the titania nanotubes. We supposed that two phenomenon occurred simultaneously during the synthesis: (i) the polymerisation ensured a coating of polyaniline on the internal surface of the titania nanotubes wall, and (ii) the titania nanotubes could act as a template to ensure production of thin, long and strained polyaniline nanofibers/nanotubes. Interactions between the organic polyaniline and the inorganic TiO₂ were suggested via H-bonding. This resulted in a lower degradation temperature for the composite compared to pure polyaniline. This phenomenon was attributed to the weakening of the polyaniline chains skeleton in the composite [10].

Interests of this new synthesis process are the tubular form of the composite at the nanoscale and the easy route to

produce it. The tubular nanostructuring of the composite permits to enhance functionalized surface in contact with molecules to be specifically adsorbed on surface compared to a spherical nanostructuring. In nanotubes both internal and external surfaces are accessible to the molecules. Another important result is the improvement of nanotubes dispersibility [10] due to the polymerisation of aniline inside the TiO₂ nanotubes either on the nanotubes walls or to produce polyaniline nanofibers/nanotubes.

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