



# Titanate nanotubes sensitized with silver nanoparticles: Synthesis, characterization and *in-situ* pollutants photodegradation



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## ABSTRACT

In this work, titanate nanotubes were modified with silver nanoparticles to produce new nanocomposite materials with enhanced photocatalytic activity for phenol removal. The TNTs were produced using a hydrothermal approach and, after being submitted to an Ag<sup>+</sup> exchange process, metallic Ag nanoparticles were obtained over the nanotubes surface. The prepared materials were structural, morphological and optical characterized by X-ray powder diffraction, micro X-ray fluorescence, transmission electron microscopy, diffused reflectance spectroscopy and X-ray photoelectron spectroscopy. The characterization results indicate that Ag<sup>+</sup> was immobilized not only in the nanotubes external surface but mainly in the TiO<sub>6</sub> interlayers space. The application of this new nanocomposite material on photocatalytic degradation of pollutants was investigated. First, the evaluation of hydroxyl radical formation, using the terephthalic acid as a probe was studied. The photocatalytic activity of the sensitized materials for phenol degradation was afterwards evaluated. The results show that the nanocomposite sample is the best catalyst, achieving 98.0% photodegradation efficiency of a 0.2 mM phenol solution within 20 min under UV–vis radiation. The reusability of the prepared samples as photocatalysts was evaluated in four successive degradation assays, using fresh phenol solutions. The sensitized sample demonstrated excellent catalytic reusability ability, without loss of photochemical stability. The structural and morphological characterization during these experiments revealed no modifications on the nanotubes morphology but a continuous increase on the Ag nanoparticles, in number and size, with the irradiation time. A mechanism for this continuous growth of the Ag nanoparticles, together with the phenol catalytic photodegradation, over the nanotubes surface, is proposed and discussed.

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## 1. Introduction

Photocatalysis has attractive potential applications in many areas such as conversion of solar energy into chemical energy (e.g., hydrocarbon/hydrogen fuel) as well as an emergent advanced oxidation technique to remove pollutants from wastewater and/or air [1,2]. Many nanocrystalline semiconductors have been explored and examined in detail for their use in this area.

Among them, TiO<sub>2</sub> has been the most promising candidate for photocatalysis applications because of its photo-stability, no toxicity, and low cost [3–5]. However, the activity of TiO<sub>2</sub> as photocatalyst is confined to UV-light radiation (less than 3% of the solar spectrum), and the photo-generated charge carriers recombination

is too high, making very difficult the practical applications of this semiconductor in this area.

Among the potential materials for TiO<sub>2</sub> replacement, titanate nanotubes (TNTs) are very interesting because they combine properties of TiO<sub>2</sub> nanoparticles (e.g. photocatalytic activity) with properties of layered titanates (e.g. ion-exchange facility) [6]. Consequently, they have the potential to be used in a wide variety of applications, including photocatalysis [7–9] dye-sensitized solar cells [10,11], optical devices [12–14], and sensors [15–17].

Nonetheless, they present some drawbacks, similar to TiO<sub>2</sub>, like the wide bandgap (ca. 3.3 eV) which strongly limits the electron-hole photogeneration under visible irradiation but lower charge recombination rate and a substantial higher surface area. Therefore, the synthesis of TNTs modified materials with a broader range of energy absorption and an even lower charge recombination degree would be an important accomplishment towards the development of more efficient photocatalyst materials.

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As a result of a synergetic combination, of TNTs with one or more components, the preparation of new materials with improved and/or innovated properties is expectable. The nanocomposite' synthesis has been one of the most popular methods for accomplish this goal [18–20]. For instance, the combination of TNTs with active photosensitizers in the visible range should result in an increase of the optical absorption of the nanocomposite material. Recently,  $\text{Sn}^{2+}$ - and  $\text{Pb}^{2+}$ -substituted  $\text{NaHTi}_3\text{O}_7$  nanotubes, obtained through ion-exchange, have been proved to be visible light' responsive and photocatalytic active for organic dyes degradation [21]. In addition, an enhancement of the TNTs photocatalytic properties through combination with other nanosized semiconductors, e.g.  $\text{Bi}_2\text{S}_3$  and  $\text{ZnS}$ , was recently reported [22]. A decrease on the photo-generated carriers' recombination rate is possible by combining TNTs with specific semiconductors, like  $\text{ZnS}$  [23]. By metal doping, e.g. by cobalt doping, it is possible to bring the nanocomposite absorption edge into the visible region and to reduce the photogenerated charges recombination rate [24].

The production of hybrid plasmonic photocatalysts using TNTs can be seen also as an interesting alternative to achieve this goal. In this context, the incorporation of metallic nanoparticles has been used to modified metal oxides materials since they act as electron traps delaying electron–hole recombination and therefore increasing the photocatalytic process efficiency. Additionally, the use of nanoparticles exhibiting surface plasmon resonance by the photocatalytic surface also generates an additional, and positive, increase in light absorption efficiency by the local electric field amplification and scattering processes [25].

Noble metals doped or deposited on TNTs are expected to have positive effects on its photocatalytic activity once they can (i) enhance the electron–hole separation by acting as electron traps, (ii) extend the light absorption into the visible range and enhance surface electron excitation by plasmon resonances excited by visible radiation, and (iii) modify the surface properties of the photocatalyst.

Studies on noble metal NPs have increased extensively due to their unique properties, which make them attractive in a wide range of applications such as optical, bio-labeling, antibacterial and (photo) catalytic applications. For instance, the modification with Ag nanoparticles leads to an increase on the photocatalytic performance and stability of  $\text{ZnO}$  films, by avoiding the semiconductor photocorrosion under UV radiation [26].

However, shape, size, dispersity and stability of the nanoparticles can be critical for their application in diverse areas. As a result, synthesis of nanoparticles with uniform morphology and high stability will be significantly beneficial for their successful applications.

In this context, various methods have been reported to synthesize silver nanoparticles on  $\text{TiO}_2$  supports by reducing  $\text{Ag}^+$  to the metallic form, including heat-induced reduction, reducing agents, photo-reduction, ionic liquids, citrate reduction, silver mirror reaction, polyol process seed-mediated growth and light (UV or gamma ray) mediated synthesis [27–31]. However, these methods are not straightforward as they use reducing agents or templates and require either high temperature or a long reaction time. Thus, new loading strategies of noble nanoparticles on titanate or  $\text{TiO}_2$  matrixes are welcome.

The biosynthesis of extracellular AgNPs with the cell filtrate of *Penicillium* sp. under light radiation has been recently reported. However, it was found that the reaction time, particle size, dispersity and stability of the synthesized AgNPs were dependent on the cell filtrate's pH [32]. Metallic Ag nanoparticles were successfully activated using a direct *in situ* electrochemical method before being supported on  $\text{TiO}_2$  for photocatalytic applications [33]. Bacterial growth inhibition was accomplished using  $\text{TiO}_2$ -Ag nanocomposites, making titania an appropriate matrix for silver

as antibacterial agent [34]. Several works related with the synthesis and photocatalytic performance of nanocrystalline Ag- $\text{TiO}_2$  and related materials have been reported, but a complete knowledge about the effective role of the metallic nanoparticles in these photoactivated processes are still missing.

This work is in line with this concern and intends to contribute to better understand the influence of the presence and amount of metallic Ag nanoparticles in the photocatalytic activity of titanate nanotubular composite materials. Phenol was chosen as model molecule for this study due to its relevance as a pollutant by itself and also as a by-product in several pollutants photodegradation processes. To achieve this goal, the synthesis and photocatalytic performance of titanate nanotubes (HTNTs) modified with crystalline Ag nanoparticles is described. This process is based on an ion-exchanged and photo-reduction step-by-step process: after hydrothermal synthesis, the HTNTs particles were first treated with an  $\text{Ag}^+$  aqueous solution to promote the metal ion immobilization; the metallic nanoparticles formation, over the HTNTs surface, was afterwards attained by UV–vis light irradiation. For the first time, and contrarily to what have been described in literature [35–37], the nanoparticles were carefully washed to eliminate some  $\text{Ag}^+$  not immobilized. Considering the photocatalytic properties of the pristine HTNTs, the evaluation of the Ag nanoparticles incorporation effect on the photocatalytic performance of this sample was evaluated through the phenol degradation. Due to the Ag nanoparticles presence, an enhancement on the Ag-HTNTs photocatalytic performance was observed. The maintenance of the photocatalytic activity of the nanocomposite, during four consecutive runs, was observed. Moreover, during these runs a continuous and unexpected formation of the Ag nanoparticles over the HTNT surface was visualized. A mechanism for the continuous Ag nanoparticles formation, during irradiation, together with their active role in the enhanced phenol photocatalytic degradation is proposed and discussed.

## 2. Experimental methods

All reagents used during this work were of analytical or chemical grade (Aldrich and Fluka) and were used as received. The solutions were prepared with distilled water.

### 2.1. HTNTs precursor synthesis

The HTNTs precursor was prepared using a procedure previously reported [38]. A titanium trichloride solution (10 wt.% in 20–30 wt.% HCl) diluted in a ratio of 1:2 in standard HCl solution (37%) was used as titanium source. To this solution a 4 M ammonia aqueous solution was added drop wise under vigorous stirring, until complete precipitation of a white solid. The resulting suspension was kept overnight at room temperature and then filtered and vigorously rinsed with deionised water in order to remove the remaining ammonia and chloride ions. The white solid obtained (precursor) was afterwards used to prepare the HTNTs sample.

### 2.2. HTNTs synthesis

Titanate nanotubes (HTNTs) were synthesized using a hydrothermal approach and a swift and highly controllable post-washing process. This synthesis was performed in an autoclave system (160 °C during 24 h) using 10 g of precursor in ca. 70 mL of a NaOH 10 M aqueous solution. After natural cooling until room temperature, the powder was washed several times with water until pH 7 on the filtrate solution. Afterwards, this powder was stirred in a  $\text{HNO}_3$  0.1 M aqueous solution for 3 h, to prepare

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