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Novel titanate nanotubes-cyanocobalamin materials: Synthesis and enhanced photocatalytic properties for pollutants removal

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ABSTRACT

New hybrid nanomaterials, with improved photocatalytic performance in pollutants removal, were obtained through the modification of titanate nanotubes (TNT) with a cobalt porphyrin, the cyanocobalamin, also knowing as vitamin B12 (B12). The nanocrystalline TNT were produced by hydrothermal treatment and after treated with cobalamin to produce B12-TNT materials. The characterization of the new hybrid material was performed by XRD, FTIR, TEM-EDS, DRS, XPS and ICP. The results show that the immobilization of the cobalt containing specie is dependent on the point of zero charge of the TNT and no modifications on the structure and morphology were observed. No significant changes in the optical band gap were observed after B12 incorporation, but an increasing in the visible light absorption, which arises from charge transfer and *d*–*d* transitions of the cobalt, was visualized. The samples photocatalytic performance was studied for the hydroxyl radical production and the highest catalytic ability was achieved by the B12-HTNT sample. The catalytic ability of these new hybrid nanomaterials for two model pollutants photodegradation, phenol and rhodamine B (RhB) was investigated. For both pollutants, the best results were achieved using B12-HTNT with a removal of 94% of a 10 ppm RhB and 87% of a 20 ppm phenol solution in 90 min of irradiation (150 mL, 0.2 g catalyst/L).

1. Introduction

Tubular nanostructures have become one of the most important research subjects in nanotechnology and related areas. Among the nanotubular materials that have been synthesised during the last two decades, titanate nanotubular structures have attracted increasing attention in recent years [1,2].

Titanate nanotubes (TNT) possess a crystalline structure very similar to TiO_2 but higher surface area, and combine the properties of conventional TiO_2, mainly photocatalytic activity, with the properties of layered titanates, *e.g.* ion-exchange ability. Additionally, TiO_2-based nanotubular structures are known to be biocompatible and nontoxic to cells and have been studied to immobilize, transport and delivery of proteins and related biological entities. For instance, studies have shown that myoglobin and cytochrome *c* can be successfully immobilized on hydrogen titanate [3].

Recently they have received increased attention due to their potential applications including photocatalysis [4], as substrate to decorate with different active catalysts [5], dye-sensitized solar cells [6] transparent optical devices [7], and sensors [8]. However these nanostructured materials can have limited applicability, *e.g.* as photoactive materials, because of their low visible radiation absorption and their high electronic recombination capability (but lower than TiO_2). Therefore, the synthesis of TNT-*based* nanomaterials with either a broader range of light absorption and/or a lower charge recombination rate would be a noteworthy achievement towards the development of successful photocatalyst materials. The combination of inorganic host lattices with organics entities, not only by intercalation but also following grafting and sol-gel procedures, have been promising synthesis methodologies for the design of new hybrid organic inorganic materials with multifunctional performance for future technological applications, including photocatalysis [9,10]. Several works have been published related with this issue including co-sensitization with semiconductor nanoparticles and zinc porphyrin [11] or phthalocyanine-sensitization [12].

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Vitamin B_{12} (B12) or cobalamin is a cobalt porphyrin which contains a cobalt ion in the center of a planar tetra-pyrrole ring, called a corrin ring, in the structure (Fig. 1).

The cobalt element can easily take their different oxidation states, where the Co^{3+} in the vitamin B12 can be reduced reversibly to Co^{2+} and further reduced to Co^{+} [13,14] making B12 an promissing electrocatalyt. Electrodes modified by vitamin B12 has shown catalytic activity for many reactions including oxidation of hydrazine [13,15], alkyl halides [16,17], cysteine [18] and oxygen reduction reaction [14,19]. Recently it has been reported the use of vitamin B12 in photoassisted processes like photocatalytic hydrogen evolution where the cobalamin acts as light harvesting unit [20], for the catalytic formation of esters and amides from trichlorinated organic compounds using vitamin B12–TiO_2 as photocatalyst [21], for modify TiO_2 nanoparticles to be used for pollutants photodegradation [22], and as modifier of Fe-doped TiO_2 to photodegradate rhodamine B (RhB) [23]. In this case, the vitamin B12 was used to induce modifications on the oxidation state of the iron ion and not directly for the dye degradation [23]. Few reports have also been published using TiO_2 as both co-catalyst and support for the cobalt complexes, including vitamin B12, regarding applications of these hybrid materials for organic synthesis [24].

TiO_2 and related compounds, including TNT, are widely used as photocatalysts because of their high photocatalytic activity, stability, non-toxicity, and low cost. Photoexcitation of TiO_2 conducts to the generation of reductive excited electrons in the conduction band (CB) and oxidative holes at the valence band (VB). Due to the reduction potential values of the excited electron and of the Co(III)/Co(I) pair on vitamin B12, a photo-induced electron transfer from TiO_2 to the cobalt ion on B12 is expected to occur. The formation of Co(II) and Co(I) catalytic species by TiO_2 irradiation activated by UV light irradiation have been reported [21,24]. Additionally, the catalytic formation of hydroxyl radicals through a hydroxocobalamin-mediated light-driven process was been recently reported [25].

Supported by these results, this work reports on the synthesis of TNT-*based* hybrid materials combining titanate nanotubes with vitamin B12, an well known cobalt-containing electrocatalytic compound, and their potential use for pollutant removal. Titanate nanotubes were prepared using a hydrothermal treatment of an Ti containing amorphous precursor [4]. The synthesis of B12-HTNT nanohybrid was accomplished by immobilization of vitamin B12 molecules, mainly by adsorption. The photocatalytic activity of the prepared samples was investigated using terephthalic acid (TA) to evaluate the capability of hydroxyl radical (•OH) photogeneration. Afterwards, the photocatalytic removal of two distinct anionic/cationic model pollutants, phenol and rhodamine B (RhB) was also evaluated.

2. Materials and methods

All reagents were of analytical grade (Aldrich and Fluka) and were used as received. The solutions were prepared with bi-distillated water.

2.1. Materials

2.1.1. TNT precursor synthesis

The amorphous precursor used for TNT synthesis was obtained using a procedure previously reported [26,27]. A titanium trichloride solution (10 wt% in HCl, 20–30 wt%) diluted in a 1:2 ratio with 2 M HCl solution, was used as titanium source. To this dark violet solution, a 4 M ammonia aqueous solution was added dropwise, under vigorous stirring, until complete precipitation of a white solid. The resulting suspension was kept overnight at room temperature and then washed with deionised water to remove the remaining ammonium and chloride ions. The white solid obtained was afterwards used to prepare the TNT sample.

2.1.2. TNT synthesis

The synthesis of the TNT sample was performed in an autoclave using 6 g of precursor in *ca.* 60 ml of NaOH 10 M aqueous solution. The sample was prepared at 130 °C during 36 h. After natural cooling until room temperature, the powder was washed several times with distillate water until pH 7 on the filtrate solution (sample NaTNT). This wet-solid, NaTNT, was also used to prepare a protonated sample (HTNT) by stirring it in a HNO_3 0.1 M aqueous solution for 2 h. Then after, the solid was washed, dried and stored.

2.1.3. TNT sensitization with the cobalt porphyrin, B12

The incorporation of the cobalt porphyrin was performed using 100 mg of NaTNT or HTNT in a B12 aqueous solution (150 mL, 150 mg L^{-1}), and stirred it for 2 h in dark conditions. The suspensions were then centrifuged and the sensitized solids washed with ultra-pure water, until removing all the un-adsorbed B12.

2.2. Photocatalytic degradation experiments

The photodegradation experiments were conducted using a 250 mL refrigerated photo-reactor [28]. A 450 W Hanovia medium-pressure mercury-vapour lamp was used as radiation source, the total irradiated energy being 40–48% in the ultraviolet range and 40–43% in the visible region of the electromagnetic spectrum.

Prior to irradiation, suspensions were stirred in darkness for 1 h to ensure adsorption equilibrium and a negative time (−10 min) was used for convenience in the figures to show the pollutant adsorption phenomenon before irradiation.

Due to their different ionic character, rhodamine B (RhB) and phenol were the pollutant molecules chosen to be degraded in this study. For the degradation experiments, suspensions were prepared by adding 30 mg of powder to 150 mL of a phenol (20 ppm) or RhB (10 ppm) aqueous solutions.

During irradiation, suspensions were sampled at regular intervals, centrifuged and analysed by UV–vis.

After centrifugation, the RhB concentration was estimated by measuring the absorbance at its chromophoric peak (520 nm). The phenol concentration variation was evaluated by electronic absorption and GC-MS.

2.2.1. Hydroxyl radical (•OH) evaluation through terephthalic acid (TA) method

The evaluation of the hydroxyl radical production was carried out using terephthalic acid (TA) as probe molecule. The radical •OH, formed during catalyst irradiation, converts the terephthalic acid into 2- hydroxyterephthalic acid (HTA), a fluorescent product easily detected and quantified by fluorescence spectroscopy. In a typical experiment, a 3 mM TA solution was prepared in 0.01 M NaOH aqueous solution. For these photocatalytic experiments, 150 mL of the TA solution and 10 mg of each powder were used, (see Section 2.2 for run details).

During irradiation, suspensions were sampled at regular intervals, centrifuged and analyzed by fluorescence spectroscopy.

2.3. Characterization

X-ray powder diffraction (XRD) was performed using a Philips X-ray diffractometer (PW 1730) with automatic data acquisition (APD Philips v3.6B), using Cu Kα radiation ($\lambda = 0.15406$ nm) and working at 40 kV/30 mA. The diffraction patterns were collected in the range $2\theta = 7–60°$ with a 0.02° step size and an acquisition time of 2.0 s/step. UV–vis absorption spectra of the solutions were