



Synthesis and characterization of one-dimensional Co-doped titanate nanostructures prepared in the presence of chitosan



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ABSTRACT

One-dimensional Co-doped titanate nanostructures with modified surface have been synthesized by alkaline hydrothermal method in the presence of bioactive natural polymer–chitosan as the organic reagent. The properties of products as-prepared and annealed under atmospheric air conditions and vacuum were studied by Raman and IR spectroscopy, SEM, HRTEM, XRD, EDX, and magnetic analysis. The results show that numerous Co-containing agglomerates of chitosan derivatives are formed on the surface of one-dimensional nanostructures when chitosan added to the reaction system with CoTiO₃ powder. An average cobalt concentration in surface formations is about 6.3 wt.% that is noticeably higher than in the body of layered structures. Magnetization measurements show a paramagnetic behavior for as-prepared products. After vacuum treatment at 600 °C and higher, the same nanostructures demonstrate the abnormal high ferromagnetic properties. Effect of chitosan as the organic reagent on texture, morphology, phase composition, and surface modification of nanostructured material is discussed.

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1. Introduction

One-dimensional TiO₂-based nanostructures have become a subject of intense research due to unique physicochemical properties and original morphology [1,2]. A large ion exchanging capacity and original shape combined with high surface area make them attractive for direct applications as photocatalysts, solar cells, magneto-optical applications, spintronic devices, ion-conducting layers, selective sorption, including radioactive ions, as well as high activity participants in fabricating delicate composites [3–8]. To control and obtain novel nanostructures, biomaterial-based templating techniques are displayed as a suitable way for the synthesis and assembly of artificial structures of crystalline inorganic materials [9]. It is known that the synergistic behavior of such the hybrid organic–inorganic materials is able to demonstrate novel interesting properties, improved characteristics, hierarchical superstructures, and versatile applications.

As diluted magnetic semiconductor (DMS), Co-doped titania has displayed interesting magnetic behavior at low cobalt

concentration [10–18]. However, the chemical nature of the ferromagnetic phase in Co-doped titania is subject to discussion. Chong et al. [16] proposed that the main factor in inducing ferromagnetic ordering is the presence of oxygen vacancies. Additionally, the crystal structure of titania plays a direct role in influencing the formation of different types of vacancy. It is therefore conceivable to manipulate the types of oxygen defect sites in Co-doped TiO₂ formations in order to achieve different magnetic/magnetization behaviors. On the other hand, Fleischhammer et al. [17] supposed that the ferromagnetism as result of substitution of Ti⁴⁺ by Co²⁺ is less feasible. The differences of the valence state and the atomic radii between Co²⁺ (0.076 nm) and Ti⁴⁺ (0.068 nm) can create a structural rearrangement to a Magneli type phase by oxygen vacancies when doping cobalt concentration is 10 at % or higher. However, such high cobalt concentration *in situ* doping has not been observed as rule. Authors proposed that under vacuum or low oxygen conditions the occurrence of metallic cobalt clusters as the origin of the ferromagnetism must be considered.

In additional, there are reports [3,8,19] that one-dimensional Co-doped TiO₂ nanostructures have been clearly shown the transparent to visible light absorption, and the enhanced antibacterial activity even in the absence of light. Therefore, they could be very promising candidates for the design of multifunctional materials, which can be extremely demanded in biology and medicine. Chitosan as the bioactive natural pharmaceutical drug used in medicine since the 19th century. It is well known [20,21]

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that chitosan-based systems have excellent biocompatibility, admirable biodegradability, ecological safety, and low toxicity combined with the versatile antimicrobial activity against a wide variety of microorganisms. In recent years, a great number of techniques have been used to design chitosan-based therapeutic systems [22]. However, chitosan has a low solubility in aqueous solutions and organic solvents which significantly limits its practical use in the preparation of modified surfaces and thin bioactive coatings. The improvement of functionality in one-dimensional nanostructured oxides by joining with bioactive organic reactants such as chitosan is especially interesting because this allows designing the hybrid organic–inorganic composites with novel properties.

In present work we have synthesized Co-doped titanate nanostructures in the presence of chitosan using alkaline hydrothermal treatment of CoTiO_3 powder. The aim of work is to study the effect of chitosan as the organic reagent on texture, morphology, phase composition, and surface modification of hydrothermal products. The hydrothermal method is one from the most commonly adopted approach for preparing one-dimensional titanate nanostructures. Besides, this method allows the chemical *in situ* reactions with organic compounds which have unique properties but the low reaction under atmospheric air conditions. On the other hand, hydrothermal method is a simple, cost-effective, nonpolluting and energy economical process which should easily be reproduced on an industrial scale.

2. Materials and methods

2.1. Basic reagents

Sodium hydroxide (NaOH), cobalt(II) titanate (CoTiO_3) and chitosan (a copolymer of *N*-acetyl-2-amino-2-deoxy- β -D-glucopyranose and 2-amino-2-deoxy- β -D-glucopyranose) were used without further purification. The nanocrystalline powder of CoTiO_3 (JCPDS, no. 15-866) was prepared by drying of the binary Co, Ti-containing hydrosol at room temperature (18–25 °C) with subsequent annealing at 1000 °C under atmospheric air pressure for 2 h. The Co, Ti-containing hydrosol was synthesized by electrochemical sol–gel method using aqueous titanium tetrachloride (TiCl_4) and cobalt(II) chloride (CoCl_2) solutions as a source of titanium and cobalt. Electrochemical synthesis was carried out similar to that described earlier by Zima et al. [23].

2.2. Synthesis of one-dimensional nanostructures

Co-doped titanate nanostructures were synthesized by hydrothermal process similar to that described earlier by Kasuga et al. [24]. Experiments were carried out as following: 0.5 g of CoTiO_3 powder was added to 30 ml of the 10 mol dm^{-3} NaOH aqueous

solution and then mixed with chitosan powder. After stirring the specimen was transferred into 40 ml a PTFE-lined autoclave and then heated at 180 °C for 24 h in an oven. The products of the hydrothermal syntheses were isolated by centrifugation and then repeatedly washed with distilled water to pH ~ 7 . The prepared samples were dried in air at 120 °C for 10 h and then annealed at 600, 800 and 1000 °C under atmospheric air pressure or vacuum ($1.33 \times 10^2 \text{ Pa}$) for 2 h.

2.3. Samples characterization

The morphology and elemental composition of as-prepared and annealed products were examined by scanning electron microscopy (SEM) using TM-1000, S-3400N (Hitachi Ltd., Japan), and transmission electron microscopy (TEM) using Technai G2 FEl. Samples for transmission electron microscopy were prepared by suspending the product in distilled water and depositing several drops on carbon coated 200 mesh copper grid, after that analysis of selected area electron diffraction patterns were performed. Elemental composition of nanostructured material was studied by energy dispersive X-ray (EDX) spectroscopy using OXFORD INCA Energy (Oxford Instruments, Ltd., GB) and SwiftTM (Hitachi Ltd., Japan). Error detection is about 10%.

The infrared (IR) absorption spectra have been recorded by an Infracam FT-801 spectrometer. The specimens were prepared as pellets with annealed KBr. Raman spectra were recorded with a RFS 100/S spectrometer (Bruker, Germany), equipped with a Nd:YAG laser operating at an exciting wavelength of 1064 nm; the laser output was 200 mW. For each spectrum, 100 scans were accumulated at room temperature. Magnetic properties were measured as a function of magnetic field in the range from 0 to 12 kOe at 80, 300, and 500 K using a Faraday magnetic balance. The X-ray power diffraction patterns of as-prepared and annealed products were recorded using D8 Advance diffractometer with monochromatic $\text{CuK}\alpha$ irradiation (Bruker, Germany) at room temperature. The data were recorded from $2\theta = 5\text{--}70^\circ$ with a step size of 0.02° (2θ).

2.4. Results and discussion

2.4.1. SEM and TEM characterization

The typical SEM images of products prepared by hydrothermal treatment of CoTiO_3 powder without additive and in the presence of chitosan are shown in Fig. 1. It should be noted that as-prepared products demonstrate common morphological features. A large number of isolated elongated rod-like nanostructures with a wide distribution of morphological parameters and random orientations are observed. Some structures have lengths exceeding several micrometers, while width is amounted several hundred of nanometers. However, the TEM images (Fig. 2) clearly show that these products are distinct from each other. As seen from Fig. 2a,

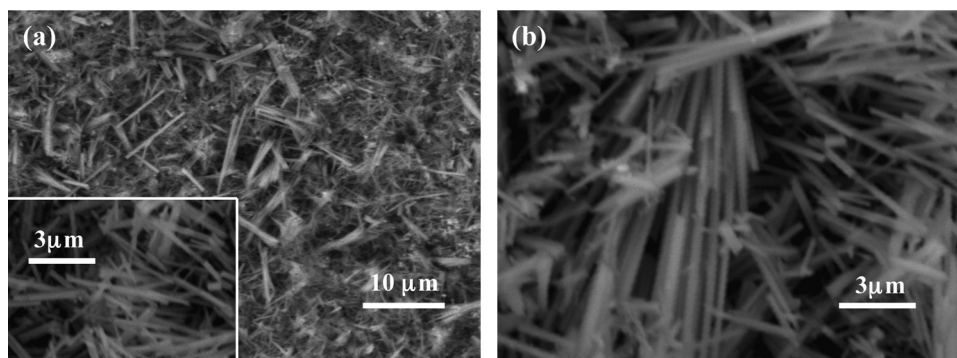


Fig. 1. SEM images of as-prepared products: (a) without additive; (b) in the presence of chitosan.

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