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SYNTHESIS AND CHARACTERIZATION OF Co^{2+} DOPED TiO_2 NANOPARTICLES

J. Kuljanin-Jakovljević[1], Z. Šaponjić[1], T. Radetić[2] and M. Radoičić[1]

[1]*Vinča Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Serbia*
[2]*Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

Abstract

Scrolled titania nanotubes were synthesized by a hydrothermal method using commercial TiO_2 powder in proton-deficient aqueous systems. In presence of $CoCl_2$ extended hydrothermal treatment of TiO_2 nanotubes lead to formation Co^{2+} doped TiO_2 nanoparticles. TEM and HRTEM measurement were used for determining the shape, dimension and structure of doped nanoaprticles. XRD confirmed anatase crystalline structure od Co^{2+} doped TiO_2. The presence of Co^{2+} ions did not induce distortions of the overall anatase crystal structure of TiO_2 matrix. The concentration of Co^{2+} ions was 1.5% compared with the amount of Ti^{4+} ions.

Introduction

Doping of wide band gap metal oxide semiconductors such as TiO_2 and ZnO with transition metal ions will influence the electronic, optical, catalytic, and magnetic properties of metal oxides. Semiconductor containing magnetic ions has been studied for several decades and has come to be known as diluted magnetic semiconductors (DMSs). More recently, interest in DMSs has turned toward their applications in spin-based electronics technologies or "spintronics"[1]. Another major category of usage dopants in semiconductor nanocrystals is that of luminescence activators. The manipulation of the luminescence properties of pure semiconductor nanocrystals by doping with ions such as Mn^{2+} or Eu^{2+} has the potential to broaden the range of useful spectroscopic properties of this class of materials. Nanostructured titanium dioxide is very well known as an ideal photocatalyst due to its photostability and high reactivity. Excitation of TiO_2 with light energy greater than its band gap (3.2 eV) generates electron-hole (e^-/h^+) pairs that can be exploited in various processes at the particle interface. Doping of TiO_2 nanocrystals with paramagnetic atoms is predicted to lead to interesting magnetic and magnetooptical behavior of nanocrystals resulting in room-temperature ferromagnetism [2]. In this work we report the synthesis and characterization of Co doped anatase nanoparticles using titania scrolled nanotubes as the starting materials.

Experimental

Titania nanotubes were synthesized by using TiO_2 (Fluka) powder as a precursor in a chemical process described elsewhere [3]. Co^{2+} doped TiO_2

nanoparticles were synthesized using hydrothermal treatment of a suspension containing $3x10^{-2}$M titania nanotubes at pH=3 as the starting material in the presence of $6.4x10^{-4}$ M $CoCl_2$. The suspension was stirred for 3h followed by 90 min hydrothermal treatment at 250°C. Nanoparticles were efficiently redispersed in water using a titanium ultrasonic bath, giving transparent colloidal dispersion of Co^{2+}doped TiO_2 nanocrystals. The sample was filtrated to remove excess Co^{2+} ions, washed and redispersed in water pH=3 or dialyzed against water pH=3 at 4°C for 3 days. The X-ray diffraction (XRD) measurements were carried out on a Philips PW-1050 (Eindhoven, the Netherlands) automatic diffractometer using CuKa radiation. Spectrophotometric measurements were carried out on a Thermo Evolution 600 UV-vis spectrophotometer. Conventional transmission electron microscopy using Philips EM-400 at 100kV was used for determining the overall shape and appearance of the particles. Atomic-resolution transmission electron microscopy investigation of doped nanoparticles was performed using HRTEM Philips CM200 (with FEG) operating at an accelerating voltage of 200kV. The percentage ratio of Co^{2+} and Ti^{4+} ions in doped nanoparticles was determined using ICP technique.

Results and Discussion

Co^{2+} were incorporated into TiO_2 nanocrystals using hydrothermal treatment of scrolled anatase nanotubes in the presence of $CoCl_2$. Titania nanotubes as axially anisotropic nano-objects, had the diameter of 12 nm. It is known that scrolled titania nanotubes, presented in Figure 1a, contain large amounts of surface Ti atoms in highly reactive undercoordinated sites that can be exploited for adsorption of Co ions.

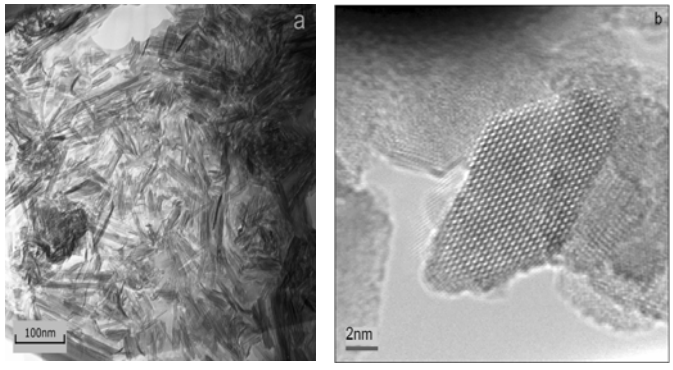

Fig. 1. a) TEM image of scrolled TiO_2 nanotubes obtained from dispersion of TiO_2 powder; b) HRTEM image of Co^{2+} doped TiO_2 nanoparticles.

Hydrothermal treatment of this composite structure results in the formation of Co^{2+} doped anatase TiO_2 nanoparticles having rhombic shape and average dimensions of 8-10 nm, Figure 1b. Particles appear to be almost defect free single

crystal. The concentration of Co^{2+} ions, determined using ICP technique, was 1.5% compared with the amount of Ti^{4+} ions in dialyzed sample. Dialysis process we used for removing of weakly bound Co^{2+} ions.

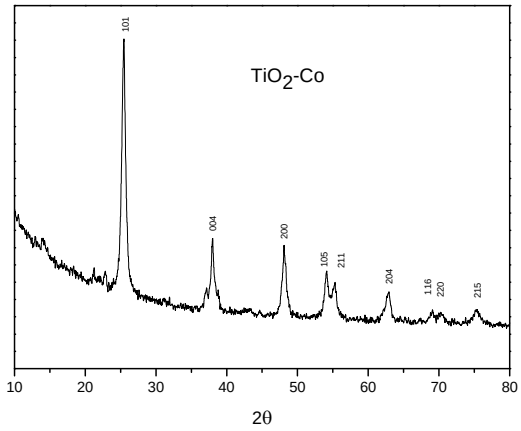

Fig. 2. XRD pattern of Co^{2+} doped TiO_2 nanocrystals

X-ray diffraction measurement of Co^{2+} doped TiO_2 nanocrystals confirmed the existence of homogeneous anatase crystal structure. The presence of Co^{2+} ions does not induced distortions of overall crystal structure. There is no indication of cobalt oxide formation. Optical properties of Co^{2+} doped TiO_2 nanoparticles are slightly changed in comparison with bare TiO_2, red-shifting the onset of absorption spectra. Doping of the core of TiO_2 nanoparticles with Co^{2+} ions, make possible synthesis of optically transparent films for the measurement of the magnetic properties.

Conclusions

We have shown that hydrothermal synthesis of Co^{2+} doped anatase TiO_2 nanoparticles using titania scrolled nanotubes as a precursor results in thermodynamically stable incorporation of Co^{2+} dopants within anatase lattice that is resistant to a "self-purification" mechanism. HRTEM analysis revealed almost defect free rhombic nanoparticles (d~8-10nm). XRD measurements of doped nanoparticles confirmed absence of any disturbance of the overall anatase crystal lattice.

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