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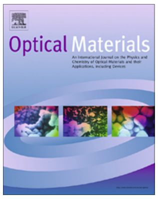

Structural phase analysis, band gap tuning and fluorescence properties of Co doped TiO_2 nanoparticles

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ABSTRACT

This paper reports on structural and optical properties of Co (0, 3, 5 & 7 mol%) doped TiO_2 (titania) nanoparticles (NPs) synthesized by employing acid modified sol–gel method. The crystalline phase of the pure and doped NPs was observed with X-ray diffraction (XRD) followed by Raman scattering technique. Field emission scanning electron microscope and transmission electron microscopy give the morphological details. Fourier transform infrared spectra indicate the bonding interactions of Co ions with the titania lattice framework. Optical studies were attained with UV–visible absorption and fluorescence emission spectroscopy. XRD analysis reveals that all prepared samples have pure anatase phase with tetragonal symmetry devoid of any other secondary phase. The average crystallite size of all samples was calculated using Scherrer's formula and was found to vary from 8 to 10 nm with doping concentration of Co. The Raman spectroscopy further confirmed the formation of TiO_2 in anatase structure in both pure and Co doped TiO_2 NPs. The most intense Raman active E_g peak of TiO_2 NPs shifted to higher energy on doping. Both UV–visible and fluorescence spectra show a blue shift in their absorption and band edge emission subsequently on increasing with Co percentage in titania host matrix, wherever there is an indication of quantum confinement effect with widening of band gap on decreasing in NPs size. There is also a possibility of strong Coulomb interaction effect on the optical processes involving the Co ions. However, the intensities of different emission spectra are not the same but decrease profoundly for doping samples due to concentration quenching effect.

1. Introduction

Scientific investigations on nanoparticles, nanocrystals, nanolayer thin films, quantum dots and quantum well, atomic and molecular clusters have grown dramatically over the past decade. A general approach in these fields is to study the optical properties of a given substance as a function of structure, size and dimensionality. When the characteristic size of the particles is comparable or smaller than its bulk Bohr exciton diameter, their optical properties become strongly dependent on size due to the quantum confinement of electrons and holes [1–5]. Recently, scholarly efforts seem to develop metal oxide semiconductor nanoparticles, which attracts a great deal of attention in terms of their potential applications in solar energy conversion and energy storage devices. Among these semiconductors, titanium dioxide is a wide band gap semiconductor and is believed to be one of the most promising known material for its high refractive index leading to a high hiding power, whiteness, resistance to photo corrosion, high dielectric constant, useful photo catalytic properties, chemical stability, low cost and non-toxicity [6–11]. These properties make this material a candidate for a large number of prime applications in many fields of chemical engineering and materials engineering including traditional catalysis or photo-catalysis, dye-sensitized solar cells, lithium insertion-based devices, integrated circuits, gas sensors, sunscreens, and in the paint industry [12]. More recently, Co doped TiO_2 generates a wide interest as diluted magnetic semiconductor (DMS) because of its ferromagnetic behaviour above room temperature for low Co doping concentration and it exhibits the Curie temperature, $T_C \sim 650$ K [13–15]. This feature makes it a promising candidate for fabricating various magneto-optical and spintronic devices.

The optical response as well as the room temperature ferromagnetism in Co doped anatase titania are affected by defect states and oxygen vacancies in the crystal lattice [16,17]. The analysis of luminescence spectrum is a cheap and effective way to study the electronic structure, optical and photochemical properties of semiconductor materials, through which the information such as

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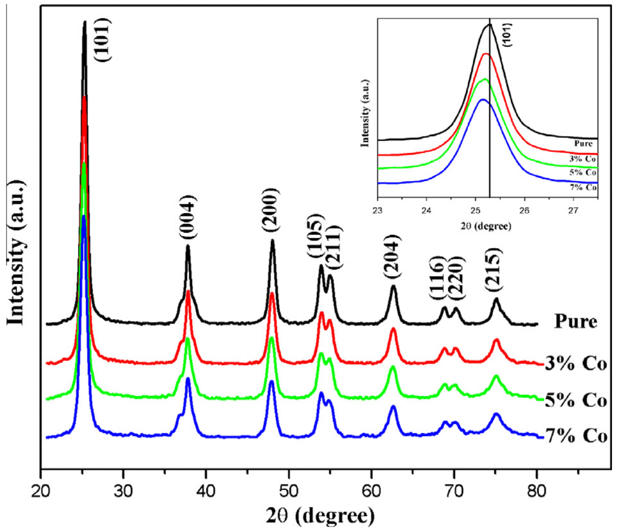

Fig. 1. XRD patterns of $Ti_{1-x}Co_xO_2$ ($x = 0.00$, 0.03, 0.05 and 0.07) NPs.

oxygen vacancies and defects, as well as the efficiency of charge carrier trapping can be understood [18,19].

Earlier investigations reported the microstructural, morphological, optical properties and luminescence performance of the transition metal doped TiO_2. Out of which luminescence performance appears to be extremely sensitive to the conditions employed during synthesis. There are hardly few papers reported on fluorescence properties of Co doped TiO_2 NPs. In the literature, it has been reported either on colloidal form of pure titania or recently few on nanocomposite forms. These factors motivated us to investigate systematically the microstructural and optical properties of Co doped TiO_2 NPs. In this communication, we have successfully synthesized nanocrystalline TiO_2 powder with low concentration of Co ions (0, 3, 5 and 7 mol%) doped by simple acid modified sol–gel method to investigate the effect of Co doping on above mentioned properties of purely anatase titania NPs. Here we have used glacial acetic acid in the conventional sol–gel method for preventing titanium (IV) isopropoxide to precipitate in water medium.

2. Experimental

2.1. Material and synthesis

NPs of Co doped TiO_2 with stoichiometric formula $Ti_{1-x}Co_xO_2$ ($x = 0.00$, 0.03, 0.05, and 0.07) were prepared by acid modified sol–gel route. All reagents used in the synthesis experiments were of analytical grade purchased from commercial sources and utilized without further purification. Titanium (IV) isopropoxide solution [$C_{12}H_{28}O_4{\cdot}Ti$] and cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$] were purchased from Alfa Aesar. Glacial acetic acid (99.9%) was obtained from Thomas Baker and absolute ethanol (99.9%) AR-grade was from Changshu Yangyuan Chemical, China.

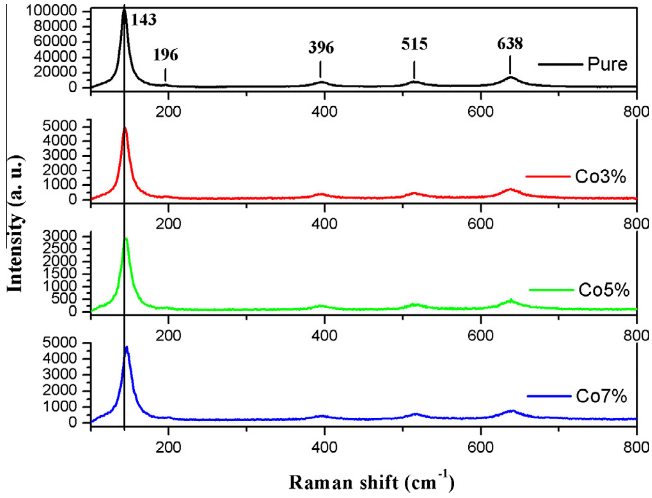

Fig. 2. Raman spectra of $Ti_{1-x}Co_xO_2$ ($x = 0.00$, 0.03, 0.05 and 0.07) NPs.

Stoichiometric amount of cobalt nitrate (the dopant starting material) was dissolved in 60 ml of deionized water at room temperature followed by an addition of 5 ml glacial acetic acid to obtain a solution say S-1. Stoichiometric amount of titanium (IV) isopropoxide was dissolved in 40 ml of absolute ethanol with constant stirring to form another solution say S-2. The solution S-2 was added drop-wise very slowly into the solution S-1 during 60 min under vigorous stirring. Subsequently, the obtained sol was stirred continuously for 2 h and was aged for 48 h at room temperature. As-prepared gel was dried for 12 h at 80 °C. The obtained solid was ground and calcined at 450 °C for 6 h (heating rate 2.5 °C/min, cooling rate 1.5 °C/min), then ground again and ready for characterizations.

2.2. Characterizations details

To confirm the formation of a single phase, X-ray diffraction (XRD) patterns of undoped and doped TiO_2 NPs were recorded with a Rigaku Miniflex-II X-ray diffractometer equipped with high intense Cu-K_α radiations ($\lambda = 1.5406$ Å) operated at a voltage of 30 kV and current 15 mA at scanning rate of 2°/min in 2θ ranging from 20° to 80°. For further confirmation of single phase, Raman spectra of all the samples were recorded at room temperature on Raman spectrometer (Renishaw, UK) with Ar ion laser of wavelength 514.5 nm and power 50 mW. Elemental compositions were known from energy dispersive X-ray spectroscopy (EDS) equipped with field emission scanning electron microscope (FESEM) from Bruker-NANO NOVA. Transmission electron microscope (TEM) micrographs and selected area electron diffraction (SAED) pattern of the prepared NPs were captured with JEOL, JEM-2010 Transmission electron microscope. The presence of different bonding vibrational frequencies were determined by a Perkin Elmer Fourier transform infrared (FTIR) spectrometer (Spectrum 2) using KBr pellets as medium. UV–visible and fluorescence emission spectra with

Table 1
Variation of crystallite size, lattice parameters and unit cell volume with doping concentration.

Co conc. (%)	Crystallite size (nm)	Lattice parameter		Unit cell volume (Å^3)	*d* value (Å) (101) plane
		a = *b* (Å)	*c* (Å)		
0	10.5	3.78733(2)	9.50845(3)	136.38796(4)	3.51698
3	9.9	3.78855(7)	9.50825(9)	136.47297(9)	3.52996
5	8.9	3.78880(5)	9.50810(2)	136.48883(7)	3.53190
7	8.7	3.78910(7)	9.50802(2)	136.50929(7)	3.53599