July - Sep © 2017 Transactions; 4(15): 576-580

International Journal of Research and Applications

ISSN (online): 2349-0020 ISSN (print): 2394-4544 http://www.ijraonline.com/

Research Article

Characterization of Cr doped TiO2 based Diluted Magnetic Semiconductor Nanomaterials

Venkateshwarlu Kalsani

Corresponding Author:
jkjagadeeshkumare@gmail.com

DOI:
http://dx.doi.org/
10.17812/IJRA.4.15(96)2017

Manuscript:
Received: 8th Aug, 2017
Accepted: 17th Sep, 2017
Published: 20th Sep, 2017

Publisher:
Global Science Publishing Group, USA
http://www.globalsciencepg.org/

ABSTRACT

Nanomaterial are most versatile and used to develop the tools widely in technical and medicinal fields. In this present scenario the synthesis, experimental and characterization techniques along with theoretical methods of Cr doped TiO2 have been reported. Thermal, microstructural, morphological, compositional, optical, dielectric and magnetic properties of Cr doped TiO2 NPs were studied. Ferromagnetism in DMSs along with the important properties and applications of TiO2 nanomaterial. The DMSs are useful class of functional materials and play a crucial role in enabling the semiconductor spintronic devices. In this paper we discuss about the synthesis and studies of Cr doped TiO2 (titania) based diluted magnetic semiconductor (DMS) nanoparticles (NPs). The doping concentration is ≤ 7 mol %. Purely single phase TiO2 based DMSs have been synthesized through wet chemical routes (acid modified sol-gel process) and these materials are in nanocrystalline form. The crystalline structure of all the samples is identified with tetragonal anatase phase with space group I41/amd. Cr doping leads to enhancement in the dielectric properties of TiO2 NPs whereas Co doping diminishes the same. These two dopings make the NPs ferromagnetic with saturation magnetization of the order of 10–3 emu/g for Cr doped while 10–2 emu/g for Co doping. In the case of 5 mol % Co doped TiO2 NPs, few beautiful spherical-flower like nanostructures with diameter of ~120 nm are observed.

Keywords: Nanomaterial, Cr doped TiO2, diluted magnetic semiconductor.

Department of Physics, KITS, Warangal, Telangana State, India - 506015.

IJRA - Year of 2017 Transactions:
Month: July - September
Volume – 4, Issue – 15, Page No's: 576-580
Subject Stream: Physics

Paper Communication: Author Direct

Paper Reference Id: IJRA-2017: 4(15)576-580

DOI: 10.17812/IJRA.4.15(96)2017

International Journal of Research and Applications
July - Sep © 2017 Transactions 4(15): 576-580

eISSN : 2349 – 0020
pISSN : 2394 – 4544
www.ijraonline.com

PHYSICS RESEARCH ARTICLE

Characterization of Cr doped TiO2 based Diluted Magnetic Semiconductor Nanomaterials

Venkateshwarlu. Kalsani
Department of Physics, KITS, Warangal, Telangana State, India - 506015.

ABSTRACT

Nanomaterial are most versatile and used to develop the tools widely in technical and medicinal fields. In this present scenario the synthesis, experimental and characterization techniques along with theoretical methods of Cr doped TiO2 have been reported. Thermal, microstructural, morphological, compositional, optical, dielectric and magnetic properties of Cr doped TiO2 NPs were studied. Ferromagnetism in DMSs along with the important properties and applications of TiO2 nanomaterial. The DMSs are useful class of functional materials and play a crucial role in enabling the semiconductor spintronic devices.

In this paper we discuss about the synthesis and studies of Cr doped TiO2 (titania) based diluted magnetic semiconductor (DMS) nanoparticles (NPs). The doping concentration is ≤ 7 mol %. Purely single phase TiO2 based DMSs have been synthesized through wet chemical routes (acid modified sol-gel process) and these materials are in nanocrystalline form. The crystalline structure of all the samples is identified with tetragonal anatase phase with space group I41/amd. Cr doping leads to enhancement in the dielectric properties of TiO2 NPs whereas Co doping diminishes the same. These two dopings make the NPs ferromagnetic with saturation magnetization of the order of 10–3 emu/g for Cr doped while 10–2 emu/g for Co doping. In the case of 5 mol % Co doped TiO2 NPs, few beautiful spherical-flower like nanostructures with diameter of ~120 nm are observed.

Keywords: Nanomaterial, Cr doped TiO2, diluted magnetic semiconductor.

1. INTRODUCTION

Research investigations on different nanostructures such as nanoparticles (NPs), nanocrystals, nanolayered thin films, quantum dots, quantum wells, atomic and molecular clusters etc. have grown dramatically over the last several years. In this direction TiO_2 (titania) nanostructures have emerged as one of the most fascinating materials in the modern era. It is well known that TiO_2 crystallizes in three different types of polymorphs: rutile, anatase and brookite [1]. It has succeeded in capturing the attention of physical chemists, physicists, material scientists, and engineers in exploring unique semiconducting and catalytic properties. A keen interest in titania has been growing because of incorporation of a suitable dopant element in this host matrix makes the former an important material for solar cells, sensors, antibacterial activities, photo catalysis, spintronic devices etc. [2-6].

The wide band gap of titania makes it a less efficient photo catalytic material in the degradation of pollutants under visible light. However, doping of a small percent of suitable foreign element enhances the visible light absorption capability by lowering the effective band gap of the material, thereby making it a visible light active photo catalyst [7]. Doping creates mid band gap electronic states that interact with the host band electrons and changes the electronic structure of the host material [8]. Among these, chromium seems to be one of the most promising dopant in TiO_2. Following the milestone work of Matsumoto *et al*. on Co doped TiO_2 systems [6], several approaches are made by different groups to increase the room temperature ferromagnetic response in this otherwise nonmagnetic TiO_2 material [9-11]. The optical response as well as the room temperature ferromagnetism of anatase Cr doped titania are affected by defect states and oxygen vacancies in the crystal lattice [12-14]. The analysis of luminescence spectrum is a cheap and effective way to study the electronic structure, optical and photochemical properties of semiconductors, through which the information such as oxygen vacancies and defects, as well as the efficiency of charge carrier trapping and recombination can be understand [15, 16].

Earlier studies report that the microstructure, morphology and optical properties of transition metal doped TiO_2 appear to be extremely sensitive to the conditions employed during synthesis. A small percent of Cr doping enhances the photo catalytic activity of titania. Apart from the existing literature, hardly few literatures report on structural refinement using Rietveld analysis on TiO_2 NPs. In the present work highly pure and stable anatase Cr (0, 3, 5 and 7 mol %) doped titania NPs have been synthesized through simple and low cost acid modified sol-gel method. Structural parameters of the synthesized NPs were refined to confirm the presence of only anatase phase and hence investigated systematically the microstructural, morphological and optical responses including fluorescence properties of the synthesized products.

2. MATERIALS AND METHOD

EDS or EDX is an analytical technique used for the compositional analysis. It is based on the analysis X-rays emitted by the sample when it is struck with charged particles. Every element has a unique atomic structure, allowing X-rays that are characteristic of the atomic structure.

Optical spectroscopy has been widely used for the characterization of nanomaterials. Infrared (IR) spectroscopy is a most popular characterization tool to measure IR frequencies absorbed by a sample when it is kept in the path of an IR radiation source. Transitions between the vibrational levels result in infrared spectroscopy of molecules. Each molecule has its own unique signatures. The information regarding structure, symmetry, bond strength, inter and intra molecular interactions etc., are obtained. FESEM is widely used technique to get topographical features, surface morphology, crystal structure, crystal orientation, presence and location of defects as well as dimension, shape and density of the particles.

Raman spectroscopy is a sensitive, fast and nondestructive technique. It is one of the most effective tools for detecting the phase, crystallinity, incorporation of dopants and the resulted defects as well as lattice disorder of the sample.

Absorption and emission spectroscopy are powerful nondestructive techniques to investigate the optical properties of semiconductors as the optical properties of semiconductor are generally determined by its electronic structure. Ultraviolet-visible (UV-vis) absorption spectroscopy is widely used to characterize organic and inorganic molecules, polymers, transition metal ions, superamolecules, nanoparticles, bulk materials, etc. Photoluminescence (PL) spectroscopy is nondestructive technique to study optical characteristic of materials. It is suitable for the characterization of both organic and inorganic materials and the samples can be in solid, liquid, or gas.

Basically, dielectric properties of the synthesized samples were studied using LCR meter (Agilent - 4285A) with two-probe setup. In the present work, morphological and microstructural features of $Ti_{1-x}Cr_xO_2$ and $Ti_{1-x}Co_xO_2$ ($x = 0.00, 0.03, 0.05$ and 0.07) NPs.

3. RESULTS AND DISCUSSIONS

Highly pure and stable (0, 3, 5 and 7 mol %) Cr doped anatase TiO_2 NPs were synthesized through low cost and simple acid modified sol-gel method. Thermogravimetric analysis shows that crystalline formation of undoped and Cr doped titania NPs is completed at ~400 ºC. The Rietveld refinement has confirmed that the Cr doped titania NPs, belong to anatase type tetragonal structure having space group ***$I4_1/amd$***. The average crystallite sizes for all the samples were calculated using Scherrer's formula and found to vary from 9-11 nm. Electron microscopies have provided the morphology and crystallinity of the NPs with particle size and distribution. Average particle size for undoped and 5 mol % Cr doped samples are found to be 12.7 and 11.6 nm respectively from TEM analysis.

Raman investigation also reconfirms the anatase phase of the synthesized products. Raman spectra reveal that characteristic intense band of TiO_2 at 143 cm^{-1} decreases in intensity and the peak position gradually shifts with increasing Cr doping concentration, which implies that the Cr incorporation in TiO_2 does not change the anatase structure but microscopic structural disorder is taking place in the periodic titanium atomic sublattices. The optical responses have been analyzed using optical absorption and fluorescence emission spectroscopies. The energy band gap of undoped titania NPs is found to be 3.25 eV as estimated from the Tauc's relation. Whereas, the band gap of the Cr doped NPs shows a widening effect and then decreases with increasing doping concentration. The fluorescence spectra show defect related visible blue emissions near 421 nm and green emission near 484 nm. Incorporation of Cr ions increases the number of non-radiative oxygen vacancies and decreases the emission intensity. Therefore, a large photocatalytic activity is expected for small amount of Cr doping in to anatase TiO_2.

The TiO_2 NPs have high dielectric constant and display a gradual dielectric relaxation in the high frequency region. The incorporation of Cr ions significantly enhances the dielectric constant as well as a.c. conductivity from that of undoped titania NPs. The loss tangent peak appearing at a characteristic frequency suggests the presence of relaxing dipoles in all synthesized samples, whereas, it increases with Cr doping and is gradually shifted towards higher frequency region. The magnetization (M-H) curve of the undoped TiO_2 NPs shows nonlinear behavior. A small hysteresis at low fields i.e. a very weak ferromagnetic (FM) signal is detected only in low field range while it is being dominated by diamagnetic (DM) order in the high field range.

The present investigations have also clearly pointed out the weak FM ordering of Cr doped NPs at room temperature which may be caused by the exchange interactions between Cr ions and oxygen vacancy in titania host lattice. In the high field region, M-H curves do not show any saturation for Cr doped TiO_2 NPs. A large amount of paramagnetic (PM) contribution to the M-H data is present. After subtraction of the PM component, Cr doped samples show ferromagnetic hysteresis loop with saturation magnetization of the order of 10^{-3} emu/g, which increases as doping Cr concentration increases. Presence of antiferromagnetic (AFM) coupling has been analyzed quantitatively with temperature dependent magnetization measurement (M-T) at a high field. The AFM coupling along with superexchange interaction reduce the magnetic moment of the Cr doped TiO_2 NPs and a weak ferromagnetism is found in the synthesized samples.

The results, presented in this report, may come up with useful guidelines for the synthesization of tunable photonic devices material, as there is an indication of simultaneous effect from quantum size confinement and creation of doner level. Enhancement in the dielectric property in Cr doped TiO_2 NPs is an additional advantage for the viewpoint of device application in nano-sized dielectric materials.

4. EXPERIMENTAL SECTION

A sol is a dispersion of the solid particles (~ 0.1–1 μm) in a liquid where the Brownian motions of the suspended particles are involved. A gel is a state where both liquid and solid are dispersed in each other. It presents a solid network containing liquid components. The liquid phase method entails a wet chemistry. It is popular in the nanoparticles synthesis and has several advantages over solid-state reaction or co-precipitation technique. Easiness of the process is one of them. Sol-gel process is cost effective and low-temperature technique. It does not need any sophisticated equipment and special environment.

Undoped and doped titania (TiO_2) nanoparticles (NPs) were synthesized by employing acid modified sol-gel method for the thesis work. Here, glacial acetic acid was used in the conventional sol-gel method for preventing titanium (IV) isopropoxide to be precipitated in water medium and make homogeneous solution of precursor and dopant starting materials. This process involves various steps like mixing, hydrolysis, densification, ageing, gelation, drying, grinding etc.

Chromium and cobalt doped TiO_2 NPs with stoichiometric formula $Ti_{1-x}Cr_xO_2$ and $Ti_{1-x}Co_xO_2$ (x = 0.00, 0.03, 0.05, and 0.07) were prepared by acid modified sol-gel route. All reagents, used in the synthesis work, were of analytical grade purchased from commercial sources and utilized without further purification. Titanium (IV) isopropoxide solution [$C_{12}H_{28}O_4.Ti$], chromium nitrate [Cr ($NO_3)_3.9H_2O$] and cobalt nitrate [Co ($NO_3)_2.6H_2O$] were purchased from Alfa Aesar used as titanium source and the dopant starting materials accordingly. Glacial acetic acid (99.9 %) was obtained from Thomas Baker and absolute ethanol (99.9 %, AR-grade).

Stoichiometric amount of chromium / cobalt nitrate was dissolved in 60 ml of deionized water at room temperature, followed by addition of 5 ml glacial acetic acid to obtain solution-1. Stoichiometric amount titanium (IV) isopropoxide was dissolved in 40 ml of absolute ethanol with constant stirring to form solution-2. The solution-2 was added drop-wise very slowly into the solution-1 within around 60 min under vigorous stirring. Subsequently, the obtained sol was stirred continuously for 2 hrs and was aged for 48 hrs at room temperature. Thereafter, as prepared gel was dried for 12 hrs at 80 ºC. The obtained solid was grinded and calcined in open air at 450 °C for 6 hrs (heating rate 2.5 °C/min and cooling rate 1.5 °C/min) followed by grinding. The samples were ready for characterizations. The undoped or pure titania was prepared using the same method for comparative study. (Table-1 & 2).

5. CONCLUSION

Highly stable (0, 3, 5 and 7 mol %) Cr doped anatase TiO_2 NPs were successfully synthesized through acid modified sol-gel method. Thermogravimetric analysis shows that crystalline formation of undoped and Cr doped titania NPs is completed at above 400 ºC. The Rietveld refinement has confirmed that whole series of the titania NPs, $Ti_{1-x}Cr_xO_2$ (x = 0.00, 0.03, 0.05 and 0.07) belongs to anatase type tetragonal structure having space group ***$I4_1/amd$***. Average crystallite size decreases on Cr doping as calculated from Scherrer's formula. Electron microscopies also provide the morphology and crystallinity of the NPs with particle size and distribution. Average particle size for undoped and 5 mol % Cr doped samples are found to be 12.7 and 11.6 nm respectively from TEM analysis. EDS result confirms the presence of the Cr in the doped TiO_2 NPs. Raman analysis gives further compliment to the phase analysis. Spectra reveal that the characteristic intense band of anatase TiO_2 at 143 cm^{-1} decreases in intensity and the peak position shifts gradually with increasing Cr doping concentration. It implies that the Cr incorporation in TiO_2 does not change the anatase structure but microscopic structural disorder is taking place in the periodic titanium atomic sublattices. The optical responses have been analyzed using optical absorption and fluorescence spectroscopies. The band gap of the doped NPs shows a widening effect and then it decreases with increasing doping concentration as estimated from Tauc's relation. The fluorescence spectra show defect related visible blue and green emissions near 421 near 484 nm respectively. Incorporation of Cr ion increases the number of non-radiative oxygen vacancies and decreases the emission intensity. So, a large photocatalytic activity is expected for small amount of Cr doping in to anatase TiO_2. The results, presented in this chapter, may come up with useful guidelines for the synthesization of tunable photonic devices material, as there is an indication of simultaneous effect from quantum size confinement and creation of doner level.

Table .1 Summary of refined structural data with crystallite size, texture and optical band gap of various Cr doped anatase titania NPs.

Parameters	**Cr concentration (mol %) in titania NPs**			
	0	3	5	7
Space group	***$I4_1/amd$***	***$I4_1/amd$***	***$I4_1/amd$***	***$I4_1/amd$***
Symmetry	Tetragonal	Tetragonal	Tetragonal	Tetragonal
$a = b$ (Å)	3.78460	3.78538	3.78610	3.78741
c (Å)	9.47232	9.47697	9.48759	9.49195
V (Å^3)	135.67391	135.79647	136.00036	136.15703
Z	4	4	4	4
Ti (4b)	(0, 1/4, 3/8)	(0, 1/4, 3/8)	(0, 1/4, 3/8)	(0, 1/4, 3/8)
O (8e)	(0, 1/4, 0.58215)	(0, 1/4, 0.58380)	(0, 1/4, 0.58418)	(0, 1/4, 0.58471)
R_p, R_{wp}, χ^2	8.17, 9.74, 2.21	5.56, 7.16, 1.26	5.59, 7.13, 1.29	5.72, 7.23, 1.36
R_B, R_F	8.56, 7.61	1.36, 0.852	1.53, 0.946	1.67, 0.991
Crystallite size (nm)	10.52	9.88	9.70	8.94
Band gap (eV)	3.25	3.58	3.43	3.38

Table .2 Compositions of undoped and 5 mol % Cr doped titania NPs by EDX technique.

Sample	Elements	Wt %
Undoped TiO_2 NPs	Ti	43.94
	O	56.06
	Total	100
5 mol % Cr doped	Ti	52.50
	O	44.99
	Cr	2.51
TiO_2 NPs	**Total**	100

REFERENCES

1) D. R. Coronado, G. R. Gattorno, M. E. Pesqueira, C. Cab, R. Coss, and R. G. Oskam, Nanotechnology **19**, 145605 (2008).

2) X. Lu, X. Mou, J. Wu, D. Zhang, L. Zhang, F. Huang, F. Xu, and S. Huang, Adv. Func. Mat. **20**, 509 (2010).

3) S. Klosek and D. Raftery, J. Phy. Chem. B **105**, 2815 (2001).

4) H. Zhang and G. Chen, Environ. Sci. Technol. **43**, 2905 (2009).

5) B. Choudhury, B. Borah and A. Choudhury, Photochem. Photobiol. **88**, 257 (2012).

6) Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Y. Koshihara, and H. Koinuma, Science **291**, 854 (2001).

7) S. In, A. Orlov, F. Garcia, M. Tikhov, D. S. Wright, and R. M. Lambert, Chem. Commun. **40**, 4236 (2006).

8) R. Long and N. J. English, Phys. Rev. B **83**, 155209 (2011).

9) J. D. Bryan, S. A. Santangelo, S. C. Keveren, and D. R. Gamelin, J. Amer. Chem. Soc. **127**, 15568 (2005).

10) B. Choudhury, A. Choudhury, P. Alagarsamy, A. Islam, and M. Mukherjee, J. Magn. Magn. Mater. **323**, 440 (2011).

11) L. H. Ye and A. J. Freeman, Phys. Rev. B **73**, 081304 (2006).

12) B. Choudhury and A. Choudhury, Mater. Sci. Eng. B **178**, 794 (2013).

13) F. D. Pieve, S. D. Matteo, T. Rangel, M. Giantomassi, D. Lamoen, G. M. Rignanese, and X. Gonze, Phys. Rev. Lett. **110**, 136402 (2013).

14) S. M. Koohpayeh, A. J. Williams, J. S. Abell, J. Lim, and E. Blackburn, J. Appl. Phys. **108**, 073919 (2010).

15) J. C. Yu, J. G. Yu, K. W. Ho, Z. T. Jiang, and L. Z. Zhang, Chem. Mater. **14**, 3808 (2002).

16) M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, and E. Giamello, J. Phys. Chem. **89**, 5017 (1985).