



Open access Journal

International Journal of Emerging Trends in Science and TechnologyIC Value: 76.89 (Index Copernicus) Impact Factor: 4.219 DOI: <https://dx.doi.org/10.18535/ijetst/v4i9.39>

Characterization of Nanocrystalline Nickel Doped Titanium -Dioxide, Synthesized by Co Precipitation Method.

Authors

R.Sivasankari¹, Dr.K.Thamizharasan^{2*}, Dr.P.Anuradha³

Mrs.R.Sivasankari, Research Scholar, R&D centre, Bharathiar University, Coimbatore.

Dr. K.Thamizharasan, Associate Professor, Dept.of Physics, Sir Theagaraya College, Chennai.

Dr.P.Anuradha, Assistant Professor, Dept.of Physics, N.K.R.Govt Arts College (W), Namakkal.

Abstract

The recent trend in the field of semiconducting technology is the fabrication of nanoscaled semiconductor devices which have diversified applications in various fields of science and technology. In the present study three different molar concentrations of Ni-doped TiO₂ nanoparticles were synthesized using co –precipitation route. The co –precipitation method, is cost effective and versatile method for the preparation of the above said nanoparticles.

X-ray powder diffraction study reveals that all the prepared samples of pure TiO₂ and nickel doped TiO₂ are crystalline structure. The average crystalline sizes of the prepared samples were calculated using Debye –scherrer formula and is found to be 19.6 nm. The Particle size for Nickel dopant TiO₂ nanoparticles was found to be between 20 nm to 21 nm. The FTIR can be used for the determination of various functional groups present in the synthesized nanoparticles. The predominant peaks confirmed the synthesized nanoparticles to be TiO₂. The nickel doping also confirmed by FTIR studies. The UV blocking property is reported using UV-visible spectroscopic studies. The energy gap is found to be 3.57eV for pure TiO₂ and it slowly increased to 4.04eV with increase in Nickel content. The surface morphology of the synthesized powders has been reported using SEM and TEM studies. The particle sizes almost coincided with the particle size calculated by Debye –scherrer. The effects of metal dopant on the structural and morphological properties have been reviewed.

Keywords: Titanium dioxide; Titanium dioxide doped with nickel oxide; Co-Precipitate method; XRD; FTIR.

1. Introduction

Titanium dioxide is a research friendly transition metal oxide exhibiting wide variety of structures, properties and phenomena. The metal oxide nanoparticles can be synthesized by various

methods, because of their low cost and ease of handling etc [1]. The properties of titanium dioxide include high refractive index, light absorption, chemical stability and relatively low-cost production [2-6].

The performance of TiO_2 based devices is largely depended on the size of TiO_2 particles which are the building units for nanoscaled devices. TiO_2 has three polymorphic forms of crystal structure namely brookite, anatase and rutile. Anatase and rutile have a tetragonal structure, whereas brookite has an orthorhombic structure. [7]. Nano Titanium dioxide particles have good electrical, optical and magnetic properties that are different from their bulk counterparts [8].

Numerous synthetic strategies such as sol-gel method, hydrothermal method, chemical vapor deposition, Pulsed laser deposition, have been developed for the fabrication of anatase phase titanium dioxide nanoparticles. [9-12].

Amongst these available methods, wet chemical route is a suitable method to control the particle size, shape, size distribution and crystalline phase. [13]. The chemical route for the production of nanocrystals allows excellent control over the mean particle size, particle size distribution, transition temperature between the different phases, physical and mechanical properties.

2. EXPERIMENTAL

2.1 Preparation of Pure and Nickel Doped TiO_2 Nanoparticles:

Titanium tetra isopropoxide (TTIP), (97.5% Sigma Aldrich), isopropyl alcohol (IPA) (99% Sigma Aldrich) and ammonia were purchased and used for the preparation of TiO_2 nanoparticles using wet chemical precipitation method. TTIP and IPA were used as the starting materials. In the synthesis by chemical precipitation method, 15ml of Titanium tetra isopropoxide was added to 100ml of isopropyl

alcohol and solution was stirred continuously for 1 hour under ambient room temperature, which was followed by addition of 15ml of ammonia solution drop by drop and was stirred continuously for 2 hours. The resultant white precipitate was collected and washed thoroughly with distilled water and ethanol to remove the impurities and un-reacted precursors. Precipitate was dried at 500°C for 1 hour.

In the synthesis of nickel doped TiO_2 , 15ml of Titanium tetra isopropoxide was added to 100ml of isopropyl alcohol and solution was stirred continuously for 1 hour under ambient room temperature. Then the dopant sources of (5%, 10%, and 15%) of nickel were added separately, which was followed by addition of 15ml of ammonia solution drop by drop to maintain the PH in the range of 9 at suitable conditions and was stirred continuously for 2 hours. The resultant green precipitate was collected and washed thoroughly with distilled water and ethanol to remove the impurities and un-reacted precursors. Precipitate was dried at 500°C for 1 hour.

The Physical examination of the sample shows very fine powder. The color of pure TiO_2 is white and Ni doped powders of different molar concentrations were found to possess pastel green color.

3. Characterization of the Synthesized Nanopowder:

The XRD pattern of TiO_2 was obtained using x-ray diffractometer by Rigaku-Dmax 2500 diffractometer with Cu-K_α in the range of $10^\circ-80^\circ$ ($\lambda=0.154\text{nm}$) The FTIR spectrum of the sample was recorded on a FTIR 8400 S series spectrophotometer at the scan rate of 25 scans/min

with 4 cm^{-1} resolution FTIR spectrophotometer. The UV-visible studies of the samples were carried out using by UV – 1700 series spectrophotometer with the slit width of 1nm. The morphologies of the prepared samples were carried out using SEM JEOL model JSM 6390. The TEM studies were carried out on the sample using JEOL model JEM 2100.

4. Results and Discussion:

4.1 XRD Analysis of Nickel Doped TiO₂

Nanoparticles with Various Nickel Concentrations: X-ray powder diffraction patterns of pure and nickel doped TiO₂ nanoparticles sintered at 500°C for various nickel concentrations is shown in figure 1.

The formed pure TiO₂ nanoparticles showed crystalline nature with 2θ peaks lying at $2\theta = 27.59^\circ$ (110), 36.12° (101), 41.29° (111), 54.46° (211) and 69.09° (301) miller planes and belong to anatase phase hexagonal structure of TiO₂. (PCPDF # 75-1537)

With the increase in nickel content the peak position got shifted to a smaller diffraction angle which is contrary to the concept already reported in the literature [14]. The crystallite sizes were calculated and estimated using Debye scherrer formula [15]

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where, K is the Scherer constant, λ is the wavelength of X-ray used for diffraction (0.154\AA), β is the full width half maximum (FWHM), and θ is the angle, the average crystallite size for pure and doped TiO₂ nanopowder are reported in table 1. All the diffraction peaks were strongly adhered to the JCPDS card no.89-1397.

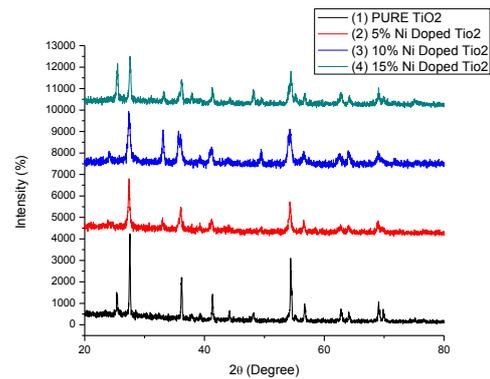


Fig 1 XRD patterns of pure and Ni-doped TiO₂.

Table 1

Summary of pure and doped TiO₂:

S.No	Samples	Particle size(nm)
1.	Pure TiO ₂	19.603
2.	5 mol% Ni-TiO ₂	20.028
3.	10 mol% Ni-TiO ₂	20.382
4.	15 mol% Ni-TiO ₂	21.455

4.2 FTIR Analysis of Nickel Doped TiO₂ Nanoparticles with Various Nickel Concentrations:

The FTIR spectra of pure TiO₂ and nickel doped TiO₂ with 5%, 10%, and 15% molar concentrations of nickel are shown in figure 2(a), (b), (c) and (d).

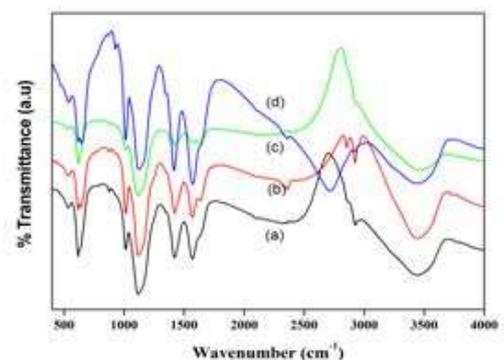


Fig.2 FT-IR spectra of (a) Pure TiO₂ (b) 5 wt % Ni doped TiO₂ (c) 10 wt % Ni doped TiO₂ (d) 15 wt % Ni doped TiO₂.

In the FTIR spectra of pure TiO₂ the sharp absorption band observed at 639.71 cm⁻¹ corresponds to Ti-O and -O-Ti-O flexion vibration [17]. The peak observed at 1141.76 cm⁻¹ corresponds to characteristic peak of pure TiO₂ as shown in the figure 2(b) [0.5% molar concentration of nickel] the peak observed at 1101.5 cm⁻¹ is the characterization peak of Nickel. [18].

The increase in nickel concentration can be clearly visualized with the increase in the intensity of the peak corresponding to nickel in the FTIR spectrum.

4.3 UV Visible Analysis of Nickel Doped TiO₂ Nanoparticles with Various Nickel Concentrations:
The small absorbance peaks were observed in the wavelength range of 250-300 nm. The number of observable peaks in the above said range has increased with the increase in concentration of nickel.

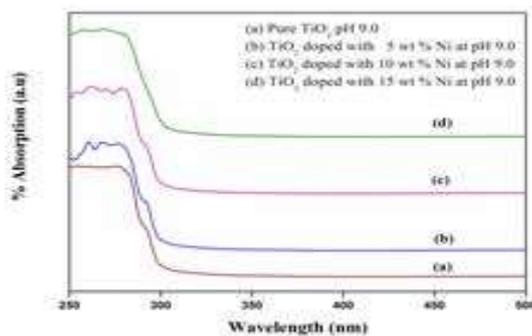


Fig 3. UV-Vis spectra of (a) Pure TiO₂ (b) 5 wt % Ni doped TiO₂ (c) 10 wt % Ni doped TiO₂ (d) 15 wt % Ni doped TiO₂.

The peaks observed in the range 250-300 nm conform the anatase phase formation which was already confirmed by XRD studies. [19]. Further the UV-blocking property of TiO₂ and nickel doped TiO₂ nanoparticles can be confirmed by absorption peaks

observed in the wavelength range of 250-300 nm which corresponds to UV-B radiation. The band gap energy is calculated using the formula $E_g = hc/\lambda$ and the results are tabulated in table 2. [20]. The UV visible studies of pure and nickel doped TiO₂ of various concentrations is shown in figure 3.

With the increase in Nickel content there is an increase in band by changing the molarities of Nickel, the band gap energy can be tailored for green energy applications.

4.4 SEM Analysis Of Nickel Doped TiO₂

Nanoparticles With Various Nickel Concentrations:

Table 2 Summary of pure and doped TiO₂:

S.No	Samples	Calcinations temperature (°C)	Band gap energy (ev)
1.	Pure TiO ₂	500	3.57
2.	5 mol% Ni-TiO ₂	500	3.97
3.	10 mol% Ni-TiO ₂	500	4.03
4.	15 mol% Ni-TiO ₂	500	4.04

The SEM images of pure and Ni doped TiO₂ of different concentrations are shown in figure 4(a), (b), (c) and (d) respectively.

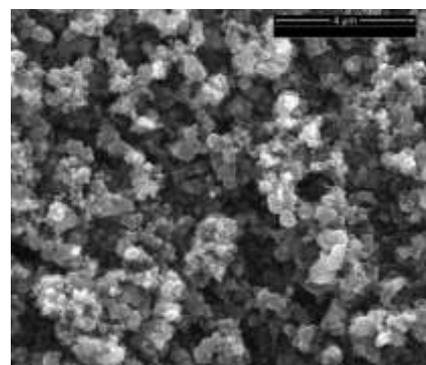
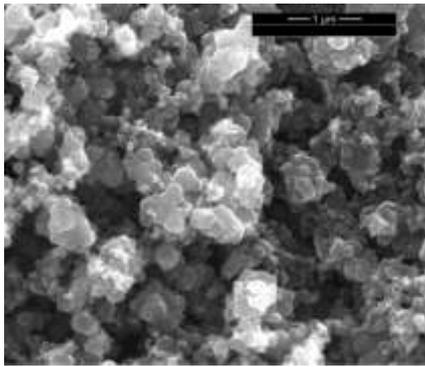
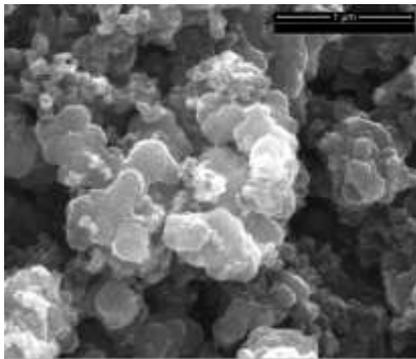
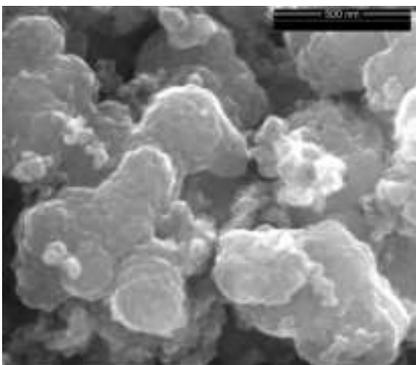


Fig 4. SEM of (a) Pure TiO₂

Fig 4. SEM of (b) 5 wt % Ni doped TiO₂Fig 4. SEM of (c) 10 wt % Ni doped TiO₂Fig 4. SEM of (d) 15 wt % Ni doped TiO₂

The surface morphology shows irregular particle shapes. The spherical shape is due to nickel and the hexagonal structure is due to the nanoparticles which have been already confirmed by XRD studies

This is approximately nearer to the particle size calculated from XRD studies. But there is an enormous variation in the case of 15% Nickel doped

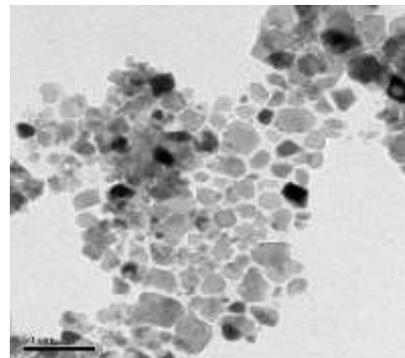
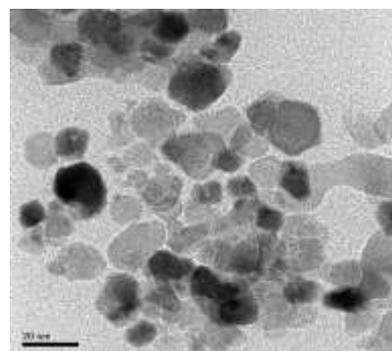
TiO₂ nanoparticles. The reason for this is due to agglomeration of nanoparticles. The agglomeration is gradually increasing with increase in nickel content. The particle sizes calculated from SEM are tabulated in table 3.

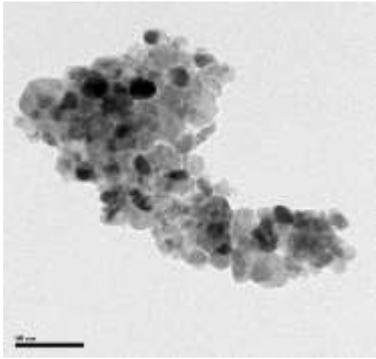
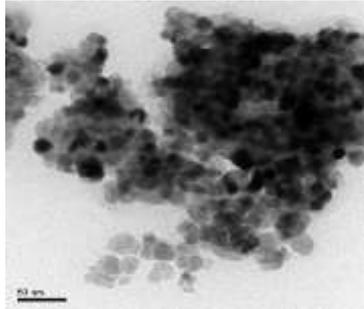
Table 3 Summary of particle size of pure and doped TiO₂ from SEM

S.No	Samples	Particle size(nm)
1.	Pure TiO ₂	25
2.	5 mol% Ni-TiO ₂	26-86
3.	10 mol% Ni-TiO ₂	21-29
4.	15 mol% Ni-TiO ₂	75-875

4.5 TEM Analysis of Nickel Doped TiO₂

Nanoparticles with Various Nickel Concentrations: The TEM images of pure and Ni doped TiO₂ of different concentrations are shown in figure 5(a), (b), (c) and (d) respectively.

Fig 5. TEM of (a) Pure TiO₂Fig 5. TEM of (b) 5 wt % Ni doped TiO₂

Fig 5. TEM of (c) 10 wt % Ni doped TiO₂Fig 5. TEM of (d) 15 wt % Ni doped TiO₂

The appearance of pure TiO₂ TEM image shows mostly hexagonal shaped crystals and some black hydrogenated nano crystals. [21]. The hexagonal structure was already confirmed by XRD studies.

With the increase in the concentration of nickel content the presence of black hydrogenated nano crystal has got increased with increased agglomeration as shown in figure 5(b), (c) and (d) respectively.

The average particle size distribution of pure and Ni doped TiO₂ nanopowder is reported in table 4.

Table 4

Summary of particle size of pure and doped TiO₂ from TEM studies:

S.No	Sample	Particle size(nm)	Reason
1.	Pure TiO ₂	8-56	Agglomeration
2.	5 mol% Ni-TiO ₂	5.8-46	Agglomeration
3.	10 mol% Ni-TiO ₂	27-74	Agglomeration
4.	15 mol% Ni-TiO ₂	64-100	Agglomeration

5. Conclusion.

The Pure and Ni-doped TiO₂ nanoparticles of different concentrations were successfully prepared by wet chemical method. XRD, UV Visible and HRTEM analysis confirmed the formation of anatase phase nanocrystallites of TiO₂. Nickel doping was clearly visualized using SEM and HRTEM studies. There is no indication of secondary phase with increase in nickel concentration because the dopant may have got incorporate into the lattice sites of TiO₂. The SEM and TEM analysis clearly confirms the agglomeration of nanoparticles. Further with increase in nickel content the agglomeration of nanoparticles have also got increased. The UV-Visible study clearly displays the UV resistant property of TiO₂ nanoparticles. The UV-blocking property clearly gets increased with increase in nickel content.

The UV-visible studies confirm that by changing the nickel content we can tailor the band gap energy and use this for solar energy applications.

References

1. M. Tomkiewicz, *Catal. Today* 58 (2000) 115.
2. A. Rammal, F. Brisach, M. Henry, C. R. Chimie, 2002, 5, 59.
3. P. V. Kamat, *Chem. Rev.*, 1999, 93, 267.
4. A. Mills, G. Hill, and S. Bhopal, I. P. Parkin, S. A. O. Neill, *J. Photochem and Photobiol. A: Chemistry*, 2003, 160, 185.
5. P. S. Awati, S. V. Awate, P. P. Shah, V. Ramaswamy, *Catal. Comm.* 4, 393.
6. R. Zhang, L. Gao, Q. Zhang, *Chemosphere*, 2004, 54, 405.
7. Xu, X. Wang and L. Zhang, "Selective preparation of nanorods and micro-octahedrons of Fe₂O₃ and their catalytic performances for Thermal decomposition of ammonium per chlorate", *Powder Technol.*, Vol. 185, No. 2, pp. 176-180, 2008.
8. S. Mahshid, M. Askar, and M. S. Ghamsari. "Synthesis of TiO₂ nanoparticles by hydrolysis and peptization of titanium isopropoxide Solution", *J. Mater. Process. Tech.*, Vol. 189, No. 1-3, pp. 296-300, 2007.
9. Xianbiao Wang, Weiping Cai, Yongxing Lin, Guozhong Wang and Changhao Liang., "Mass production of micro/nanostructures porous ZnO plates and their strong structurally enhanced and selective adsorption performance for environmental remediation", *J. Mater. Chem.*, 20, 8582-8590, 2010.
10. T. Trung, W. J. Cho, C. S. Ha, *Mater. Lett.* 57 (2003) 2746.
11. C. H. Lu, M. C. Wen, *J. Alloys Compd.* 448 (2008) 153.
12. D. Byun, Y. Jin, D. B. Kim, J. K. Lee, D. Park, *J. Hazard. Mater.* 73 (2000) 199.
13. E. Gyorgy., E. G. Socol, E. Axente, I. N. Mihailescu., C. Ducu, S. Ciuca, *Appl. Surf. Sci.* 247 (2005) 429.
14. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley, Reading, MA, 1987, p. 294.
15. R. Jenkins. and S. Snyder. L. r, "Introduction to X-ray powder diffractometry", J. K. Winefordner, Ed., p. 89, John Wiley & Sons, New York, NY, USA, 1996
16. Chang Sung Lim, "Synthesis and characterization of TiO₂-ZnO nanocomposite by a two-step chemical method", *Journal of Ceramic Processing Research*, 11, 631-635, 2010.
17. J. A. Wang, Ballesteros R. L. Lopez. T., A. Moreno, R. Gomez, O. Novaro, X. Bokhimi, *J. Phys. Chem. B* 105 (2001) 9692.
18. L. J. Chen, Li G. S., L. P. Li, *J. Therm. Anal. Calorim.* 91 (2008) 581.
19. "International journal of engineering text" "11(2013).
20. "Synthesis and characterization of nano-TiO₂ via different methods" "R. Vijayalakshmi and V. Rajendran, *Archives of Applied Science Research*, 2012, 4 (2):1183-1190.