

ENHANCEMENT IN OPTICAL PROPERTIES OF COBALT DOPED TiO₂ NANOPARTICLES

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Cobalt doped titanium dioxide has consumed great consideration because of their photo catalytic activity and numerous utilizations in paints, white pigments and tooth paste. The co-precipitation technique was utilized in this present study to produce titanium dioxide nanoparticles using (TTIP) titanium tetra iso-propoxide and cobalt nitrate as a starting precursor. Cobalt doped TiO₂ nanoparticles were synthesized up to four to seven percent of cobalt composition. The Morphology of nanoparticles, crystal structure and optical characteristics were analyzed by XRD, UV-vis spectroscopy and scanning electron microscopy, respectively. Functional groups of cobalt doped TiO₂ nanoparticles were confirmed by Fourier transform infrared spectroscopy (FTIR). The modified cobalt-doped titanium dioxide exhibits increased absorption in UV region as increasing cobalt content. The main purpose of this research is to enhance the photo catalytic activity and observe the dimensions, morphology and cobalt concentration as well as shape of prepared nanoparticles.

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1. Introduction

TiO₂ is undeniably an excellent photo catalyst because of its desirable properties [1], including chemical stability [2], resistance to photo corrosion [3], non-toxicity [4] and high oxidation strength [5]. Titanium dioxide has been utilized in different manufacturing and cosmetic applications due to its distinctive elemental characteristics. This semiconductor material has a refractive index greater than the other compounds. This enables titanium dioxide to have a brilliant and splendid feature. As titanium dioxide has the capability to significantly absorb ultra violet light, so that's why it has been used as a substantial sunscreen for many years [6][7]. TiO₂ nanoparticles are also having much important utilization in photovoltaic cell, gas sensors, photo electrodes, and high efficiency photo cells and in treatment of cancer [8]. There are three major crystalline forms of titanium dioxide, anatase, rutile and brookite. Anatase is very common and stable phase at room temperature in nanomaterials [9]. Due to high refractive index it is used in gas sensors, solar cells, and multilayer optical coatings [10]. Thermodynamically, at all temperature's rutile is the most stable polymorph of titanium dioxide. Nano-scale rutile components are translucent to visible light, yet they are highly effective in ultraviolet wave absorption. Nano-sized rutile particles that absorb UV radiations exhibit blue shift as compared to bulk rutile, so that higher energy UV radiations are absorbed by the nano sized rutile particles. Rutile (3.0 eV) has narrow band gap than anatase (3.2eV) of titanium dioxide [11]. That is the reason they are utilized for the most part in sunscreens to ensure against UV incited skin harm. Both rutile and anatase have tetragonal structure. Brookite is metastable phase of titanium dioxide and immediately changed into rutile while heating and it has orthorhombic structure [12]. In rutile,

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the linear chains of two octahedra edges are shared in [0 0 1] direction and through corner-shares bonding TiO_6 chains are connected to each other. In the anatase, each octahedron has a four-sided arrangement with the other four octahedra leading to zigzag pattern and in brookite, each octahedron shares three edges and these octahedral arrangements generate a crystalline structure [13]. Titanium dioxide nonmaterial usually is translucent in the visible light. It is possible to enhance the optical sensitivity and activity of titanium dioxide nanomaterials in the visible light region by doping or sensitization. Material efficiency of TiO_2 can be improved by optimizing structural and optical characteristics. In this research cobalt is used as dopant element because cobalt provides additional energy in band gap of TiO_2 [19]. There were many techniques to produce nanoparticles including sol gel, hydrothermal, spinning, co-precipitation, chemical vapor deposition and pyrolysis and biosynthesis methods. Co-precipitation method is most effective, cost effective and time saving method as compared to other techniques for preparation of cobalt doped TiO_2 nanoparticles. The aim of this research is therefore to study the impact of co-additives on the structural and optical characteristics of TiO_2 nanoparticles.

2. Experimental

Titanium tetra-iso-propoxide (TTIP), ethanol, Cobalt nitrate and ammonia were purchased from Sigma Aldrich. Ammonia was used as a precursor in this research work. Cobalt doped TiO_2 nanoparticles were prepared with different concentration ($\text{Ti}_{(1-x)}\text{Co}_x\text{O}_{2x} = 0.04, 0.05, 0.06, \text{ and } 0.07$) by co-precipitation method. For example, at room temperature, 16 ml of ethanol mixed with 8ml of titanium tetra iso-propoxide (TTIP) and stirred it for 15 minutes to make solution A. For solution B, desire amount of cobalt nitrate [$\text{Co}(\text{NO}_3)_2$] (4%, 5%, 6% and 7%) mixed with 16 ml of ethanol and solution B was also stirred for 15 minutes. Solution A and solution B was mixed under continues stirring. To maintain pH at 9, few drops of ammonia solution were added. The stirring was stopped as pH approached at 9, after that sample had kept for aging for 12 hours. After becoming the precipitate, Sample was washed with distilled water several times to reduce contamination and unwanted impurity until pH become neutral. For twelve hours the specimen was dried at 100 °C. Dried sample was grinded carefully. After this stage, sample was baked at 500 °C for two hours. Finally, cobalt doped titanium dioxide nanoparticles in light green color were obtained. Cobalt doped TiO_2 nanoparticles with anatase and rutile phases were characterized with XRD, SEM, FTIR and UV-vis spectroscopy. The crystalline of cobalt doped TiO_2 nanoparticles was analyzed through XRD technique *using Cu Ka radiation source*. FTIR was used to investigate chemical structure of co-doped TiO_2 nanoparticles. Absorption with different wavelength was observed by UV spectroscopy.

3. Results and discussion

XRD pattern of cobalt doped TiO_2 nanoparticles with various concentrations (4%, 5%, 6% and 7%) is shown in Fig. 1. Main diffraction peaks (101), (110), (121), (103), (201), (211), (220), (221) and (215) are at around 25.42° 27.2°, 30.08°, 35.04°, 45°, 54.08° 56.48°, 66.48° and 75.3° respectively. This phenomenon verified that dopants are well distributed with in matrix of TiO_2 .

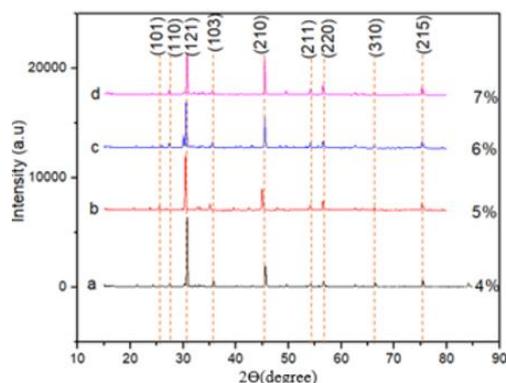


Fig. 1. XRD pattern for $Co_xTi_{(1-x)}O_2$ nanoparticles.

Three types of phases were observed, anatase, brookite and rutile are shown in Fig. 1. The main peak (brookite) was observed at 30.08° having hkl value (121). Remaining peaks of anatase and rutile were noticed at 25.42° 35.04° , 66.08° , 75.45° and 27.2° , 45.56° , 54.18° , 56.58° with hkl values (101), (103), (221), (215) and (110), (201), (211), (220) respectively. As concentration is increased, anatase and rutile peaks were started to appear in XRD pattern. Any peak of cobalt was not recognized in XRD pattern at any concentration during whole process. However, the sharp level of diffraction peak increased (FWHM value was decreased) as doping levels increased. This was primarily due to Co has lower atomic radius than Ti. All peaks are matched with JCPDS card 29-1360 and 21-1272. The average particle size of Co doped TiO_2 nanoparticle size is 42.63nm, 38.81nm, 41.30nm and 40nm. Average crystal size of all the samples changed irregularly as amount of cobalt is increasing.

The average size was calculated from x ray diffractions by taking all the 2Θ values using eq. (1) (Scherer's equation)

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

where D is crystalline size, β is a full width half maximum, Θ is a reflection angle= 0.154178 nm and K is shape factor. Volume Percentage of anatase brookite and rutile phase which are present in XRD pattern can be measured through equation (2), (3) and (4)

$$f_A = \frac{I_A}{I_B + I_A + I_R} \quad (2)$$

$$f_B = \frac{I_B}{I_A + I_B + I_R} \quad (3)$$

$$f_R = \frac{I_R}{I_A + I_B + I_R} \quad (4)$$

where I_A , I_B and I_R are the maximum intense peaks of anatase, brookite and rutile phase. As per calculations, anatase = 7.20 %, brookite = 70.72 % and rutile = 22.07 % present in XRD pattern. According to above measurements maximum number of particles having brookite phase and minimum number of particles having structure like anatase.

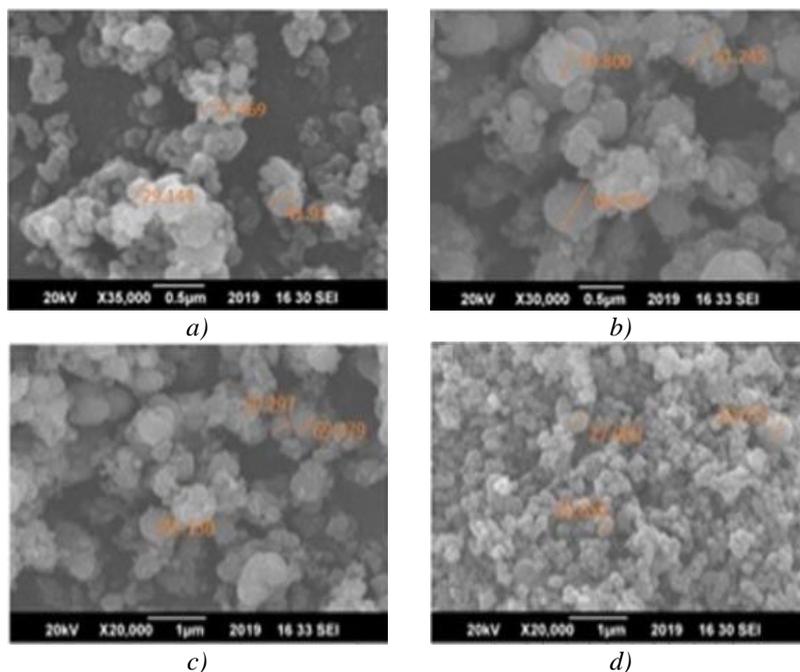


Fig. 2. SEM micrographs (a-d) for $Co_xTi_{(1-x)}O_2$ nanoparticles.

Scanning electron microscope is used to investigate the morphology and composition of nanoparticles. Fig. 2 show that the particles which were made with different concentrations of cobalt (4 %, 5 %, 6% and 7 %) showed conspicuous agglomeration. Most of the particles seem spherical in shape, show, irregular and non-uniform grain size distribution. Spherical shape is significant not only for the design of surface area and surface properties, but also for change the electronic structure. Size of particles also varied with doping amount of cobalt. Particle size of TiO_2 was slightly decreased as amount of dopant element (cobalt) was increased. The Incorporation of cobalt ions in the lattice sites has changed the complete morphology of TiO_2 samples. Average particles size of nanoparticles is 60 nm, 32.84 nm, 35.40 and 22.59 nm respectively and these results are aligning well to that of the XRD crystallite size.

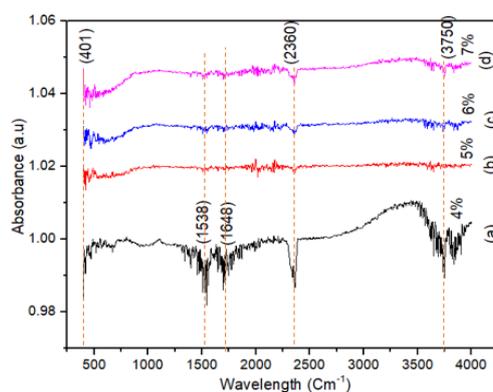


Fig. 3. FTIR spectra for $Co_xTi_{(1-x)}O_2$ nanoparticles.

FTIR spectra of $Ti_{(1-x)}Co_xO_2$ ($x = 0.04, 0.05$ and 0.06 and 0.07) nano particles at room temperature was noted and various bands are shown in Fig. 3 by dashed lines. Normally FTIR is used to analyze the functional groups, Vibrational modes, geometry and inter interactions of molecules. A small absorption peak 401cm^{-1} to 409cm^{-1} is attributed to Ti-O-Ti vibrations [16]. The shifting of peak from 401cm^{-1} to lower wave number 409cm^{-1} may be due to substitution of

cobalt ion on lattice of Ti^{4+} . The absorption peaks appearing at 1538 cm^{-1} is attributed to H-O-H bond of adsorb water. Peak observed at 2360 cm^{-1} is due to stretching mode of $O=C=O$ being trapped with TiO_2 [17]. Peak positioned at 1648 cm^{-1} is due to the bending mode of hydroxyl group of TiO_2 [18]. The peaks around at 1748 cm^{-1} and 1772 cm^{-1} are assigned as residual organic species which may not be removed by distilled water. Peak comes out at 3750 cm^{-1} is due to stretching mode of OH group on surface of TiO_2 . Lower intensity peaks positioned at 1396 cm^{-1} and 1457 cm^{-1} in specimens are due to the anion CO_3 and $O=C=O$ which comes from environment during synthesis and doping process [19]. It was observed that optical characteristics rely on the inner electronic structures of nanoparticles. Research into the optical characteristics of nanoparticles can therefore provide us with a dedicated knowledge of their semiconductor properties.

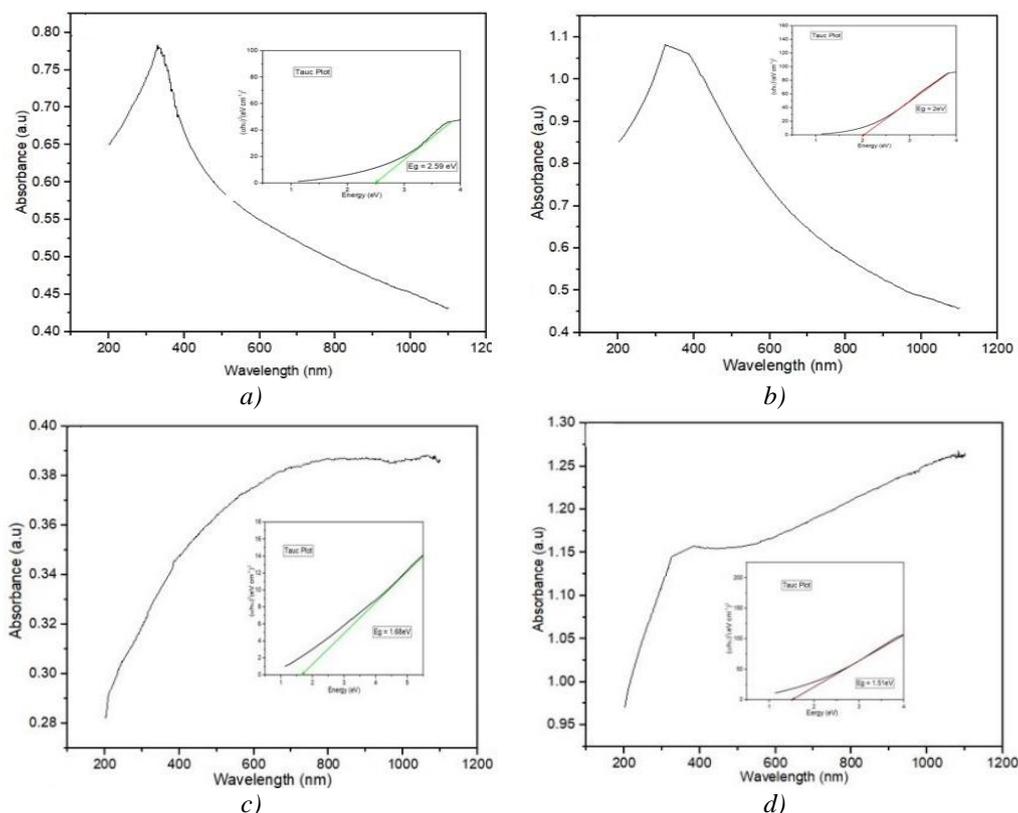


Fig. 4. UV-Visible absorption spectra (a-d) for $Co_xTi_{(1-x)}O_2$ nanoparticles.

Fig. 4 shows that absorbance was occurred in ultraviolet region but as concentration was increased absorbance was shifted towards visible region. The typical absorbance was noticed at wavelength, 329nm, 341nm, 348 nm and 353 nm respectively. Slight red shift in $Co-TiO_2$ nanoparticles can be explained due to sp-d exchange interactions between the band electrons and the localized d electrons of the Co^{2+} ions substituting Ti^{4+} cations. The interactions of the p-d and s-d exchange lead to upward transformation of the valence band edge and downward transition of the conduction band edge which result in a reduction of band gap. Using Tauc equation, band gap energy can be calculated. Estimated band gap of cobalt doped TiO_2 nanoparticles was 2.5eV, 2.0 eV and 1.5 eV respectively. As wavelength was increased, band gap shifted towards small values that's mean photo catalytic activity can be increased. There is another reason for huge reduction in band gap energy. As concentration is increased band gap is decreased due to presence oxygen vacancies which form of large number of mid band gap states under the conduction band [15].

These mid band gap states make TiO₂ as good absorbing material in visible region. Tauc relation is given below in equation (5)

$$\alpha hv = A(hv - E_g)^{n/2} \quad (5)$$

In above equation, h is planks constant (6.626176×10^{-34} joule-seconds), v is incident photon frequency, α is coefficient of absorption, A is general constant, E_g is band gap energy and n depend on nature of transition. Absorption coefficient from following equation can be calculated from equation (6)

$$\alpha = 2.30 \left(\frac{Ab}{t} \right) \quad (6)$$

Estimated band gap of cobalt doped TiO₂ nanoparticles was 2.59eV, 2.0eV, 1.68 eV and 1.5 eV respectively. As wavelength was increased, band gap shifted towards small values that's mean photo catalytic activity can be increased. The reduction in band gap proved that dopant element (cobalt) was well dispersed on matrix of TiO₂.

Cobalt concentration (%)	Absorption wavelength (nm)	Band gap energy (eV)
4	329	2.59
5	341	2.0
6	348	1.68
7	353	1.51

4. Conclusions

Cobalt doped TiO₂ nanoparticles have successfully synthesized by co-precipitating method using TTIP and cobalt nitrate (4%, 5%, 6% and 7%) as precursors. Mixture of phase's brookite, anatase and rutile were obtained. The resulting products have been characterized by XRD, SEM, FTIR and UV-vis spectroscopy respectively. XRD results confirm the crystal structure and presence of anatase, brookite and rutile phase with particle size in range of 43.63 nm to 38.81 nm. Functional groups were identified by Fourier transform emission spectroscopy.

Through Scanning Electron Microscopy, it was revealed that the change in morphology increased with the increased in the amount of cobalt in TiO₂. As concentration was increased absorption was shifted towards visible region. Same as band gap was also decreased as percentage of doping element cobalt is increased. The reduction of band gap also due to the formation of large number of mid band gap states. From above results it was observed that doping of cobalt plays important role in improvements of crystal structure, morphology of particles and photo catalytic activity in visible region.

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