#### ORIGINAL ARTICLE

# Synthesis and characterization of undoped and cobalt-doped TiO<sub>2</sub> nanoparticles via sol-gel technique

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Abstract TiO<sub>2</sub> nanoparticles doped with different concentrations of cobalt (4, 8, 12 and 16 %) were synthesized by sol-gel method at room temperature with appropriate reactants. In general, TiO<sub>2</sub> can exist in anatase, rutile, and brookite phases. In this present study, we used titanium tetra iso propoxide and 2-propanol as a common starting materials and the obtained products were calcined at 500 °C and 800 °C to get anatase and rutile phases, respectively. The crystalline sizes of the doped and undoped TiO<sub>2</sub> nanoparticles were observed with X-ray diffraction (XRD) analysis. The functional groups of the samples were identified by Fourier transform infrared spectroscopy (FTIR). From UV-VIS diffuse reflectance spectra (DRS), the band gap energy and excitation wavelength of doped and undoped TiO<sub>2</sub> nanoparticles were identified. The defect oriented emissions were seen from photoluminescence (PL) study. The spherical uniform size distribution of particles and elements present in the samples was determined using two different techniques viz., scanning electron microscopy (SEM) with energy-dispersive spectrometer (EDX) and transmission electron microscope (TEM) with selected area electron diffraction (SAED) pattern. The second harmonic generation (SHG) efficiency was also found and the obtained result was compared with potassium di hydrogen phosphate (KDP).

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## Introduction

Titanium dioxide or titania (TiO<sub>2</sub>) was first produced commercially in 1923. It is obtained from a variety of ores. The bulk material of TiO<sub>2</sub> is widely nominated for three main phases of rutile, anatase and brookite. Among them, the TiO<sub>2</sub> exists mostly as rutile and anatase phases which both of them have the tetragonal structures. However, rutile is a high-temperature stable phase and has an optical energy band gap of 3.0 eV (415 nm), anatase is formed at a lower temperature with an optical energy band gap of 3.2 eV (380 nm) and refractive index of 2 (Thamaphat et al. 2008). Among these polymorphs, rutile and anatase have been widely studied. Brookite is rarely studied due to its complicated structure and difficulties in sample preparation (Hu et al. 2009). These three phases can be commonly described as constituted by arrangements of the same building block-Ti-O<sub>6</sub> octahedron in which Ti atom is surrounded by six oxygen atoms situated at the corners of a distorted octahedron. In spite of the similarities in building blocks of Ti-O<sub>6</sub> octahedra for these polymorphs, the electronic structures are significantly different (Guangshe et al. 2011). Photocatalysis using TiO<sub>2</sub> as a catalyst has been widely reported as a promising technology for the removal of various organic and inorganic pollutants from contaminated water and air because of its stability, low cost, and non-toxicity (Liu et al. 2008).

 $TiO_2$  is the promising material as semiconductor having high photochemical stability and low cost. Well-dispersed titania nanoparticles with very fine sizes are promising in



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many applications such as pigments, adsorbents, and catalytic supports (Ramakrishna and Ghosh 2003).

Since Fujishima and Honda discovered the photocatalytic splitting of water on a  $TiO_2$  electrode under ultraviolet (UV) light, many synthesis methods for preparing  $TiO_2$  nanoparticles and their applications in the environmental (photo catalysis and sensors) and energy (photovoltaics, water splitting, photo/electrochromics, and hydrogen storage) fields have been investigated (Shan and Demopoulos 2010). Recently, fine particles of titania have attracted a great deal of attention, because of their specific properties as an advanced semiconductor material, such as a solar cell, luminescent material, and photocatalyst for photolysis of water or organic compounds and for bacteriocidal action (Sugimoto et al. 2003).

The Co-doped  $\text{TiO}_2$  nanocrystals have consumed great attention due to its enhanced photocatalytic activity (Yang et al. 2007). In this paper, we report the preparation of different weight percentages of Co-doped  $\text{TiO}_2$  nanoparticles by a sol–gel route.

#### Materials and methods

## Sample preparation

# Preparation of bare and cobalt-doped TiO<sub>2</sub> nanopowder

Sol–gel technique was used to prepare bare and cobaltdoped TiO<sub>2</sub> samples. 90 ml of 2-propanol was taken as a primary precursor and 10 ml titanium tetra isopropoxide was added to it drop wise with vigorous stirring during the process of TiO<sub>2</sub> formation. The solution was vigorously stirred for 45 min to form sols. Liquid solution cobalt nitrate of desired concentration (4, 8, 12, and 16 %) was poured slowly drop by drop to that mixture with continued stirring. To obtain nanoparticles, the obtained gels were dried at 80 °C for 5 h to evaporate water and organic material to the maximum extent. Finally, the powders were kept in muffle furnace and calcinated at 500 °C for 5 h for the harvest of anatase phase and 800 °C for rutile phase. The particle was pulverized to powder using an agate mortar at room temperature for further characterizations.

#### Sample characterization

The bare and Co-doped  $TiO_2$  anatase are subjected into different characterizations, such as powder XRD, FTIR, UV-DRS, PL, SEM with EDX, TEM with SAED pattern, and SHG (NLO). The crystalline phase and particle size of  $TiO_2$ nanoparticles were analyzed by X-ray diffraction (XRD) measurement, which was carried out at room temperature using XPERT-PRO diffractometer system (scan step of



0.05°, counting time of 10.16 s per data point) equipped with a Cu tube for generating Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The incident beam in the 2-theta mode over the range of 20°-80°, operated at 40 kV and 30 mA. The chemical structure was investigated by AVATAR 330 Fourier transform infrared spectrometer (FTIR) in which the IR spectrum was recorded by diluting the mixed powder in KBr and in the wavelength between 4,000 and 400  $\text{cm}^{-1}$ . The band gap energy and the particle size were measured at wavelength in the range of 200-2,500 nm by UV-VIS-NIR spectrophotometer (varian/carry 5000) equipped with an integrating sphere and the baseline correction was performed using a calibrated reference sample of powdered barium sulfate (BaSO<sub>4</sub>). The photoluminescence spectra (PL) are recorded with Perkin Elmer LS fluorescence spectrophotometer. Scanning electron microscope (SEM) images were observed with a Hitachi S-4800 microscope, combined with energydispersive X-ray spectroscopy (EDX, Oxford 7021) for the determination of elemental composition. Transmission electron microscope (TEM) with selected area electron diffraction (SAED) images were taken using a technai t20 operated at a voltage of 200 kV. The NLO property of the materials was confirmed by the Kurtz powder second harmonic generation (SHG) test. A Q-switched Nd-YAG laser whose output was filtered through 1,064 nm narrow pass filter was used for this purpose. The input power of the laser beam was measured to be 4.5 m J/pulse.

## **Results and discussion**

Powder X-ray diffraction study (XRD)

Figure 1 exhibits the XRD patterns of bare and cobaltdoped  $TiO_2$  nanocrystals calcined at 500 °C for 5 h. From



Fig. 1 X-ray diffraction pattern for bare  $\rm TiO_2$  and Co-doped  $\rm TiO_2$  nanoparticle

Table 1 Crystallite sizes for the bare and Co-doped  ${\rm TiO}_2$  nanoparticle

Samples	Crystallite size (nm)		
Bare TiO <sub>2</sub>	15.31		
4 % Co-doped TiO <sub>2</sub>	19.9092		
8 % Co-doped TiO <sub>2</sub>	20.9140		
12 % Co-doped TiO <sub>2</sub>	23.4380		
16 % Co-doped TiO <sub>2</sub>	25.9223		

the diffraction patterns, it is noted that bare and cobaltdoped TiO<sub>2</sub> are in anatase phase rather than rutile or brookite (JCPDS Card no 21-1272). The XRD patterns obtained in the present study are identical with the earlier report (Karthik et al. 2010). At low level of cobalt incorporation, the XRD patterns do not show any cobalt phase, indicating that cobalt ions are uniformly dispersed on the host TiO<sub>2</sub>. However, at high level of Co<sup>2+</sup> incorporation (12 and 16 wt%), peaks related to cobalt are started to appear which are marked by a symbol star.

From the obtained peaks, the average nanocrystallite size was measured according to using Debye–Scherrer formula, the Eq. (1).

$$D = \frac{K\lambda}{\beta \text{Cos}\theta} \tag{1}$$

where *D* is the crystallite size, *K* is the shape factor,  $\lambda = 0.154 \text{ nm}$ ,  $\beta$  is the full width at half maximum,  $\theta$  is the reflection angle and the results are presented in Table 1. In comparison with undoped TiO<sub>2</sub>, all the doped products show increased particle size. The increased particle size may be explained by the fact that the ionic radius of Co<sup>2+</sup> (0.74 Å) is greater than that of Ti<sup>4+</sup> (0.60 Å) (Liu et al. 2008).

Fourier transform infrared spectroscopy (FTIR)

Figure 2 shows the FTIR spectra of the obtained bare and Co-doped TiO<sub>2</sub> nanoparticles after calcined at 500 °C for 5 h. The peak positioned at 3,415  $\text{cm}^{-1}$  is attributed to O-H stretching vibration. The peaks appearing at 1,629  $\text{cm}^{-1}$ were attributed to H-O-H bending vibration mode of physically observed water. Appearance of Ti-O-Ti frequency absorption is noted between 600 and 400  $\text{cm}^{-1}$ (Choudhury and Choudhury 2012). The appearance of band at  $2,860 \text{ cm}^{-1}$  was due to the C-H bond of the organic compounds (Maensiri et al. 2006). The weak band at 2,833  $\text{cm}^{-1}$  could be ascribed to the characteristic frequencies of residual organic species, which was not completely removed by ethanol and distilled water washing (Guo et al. 2007; Wang et al. 2007). The two prominent absorption bands at 3,400 and 1,633  $\text{cm}^{-1}$  in the materials can be recognized as the stretching and bending vibrations



Fig. 2 FTIR spectra pattern for bare  ${\rm TiO}_2$  and Co-doped  ${\rm TiO}_2$  nanoparticle



Fig. 3 UV-DRS spectra for bare  $TiO_2$  and Co-doped  $TiO_2$  nanoparticle-direct transition

of water molecules. The intensity of these two bands in Co is diminished compared with bare TiO<sub>2</sub>. The peaks in between 2,924 and 2,843 cm<sup>-1</sup> are assigned to C–H stretching vibrations of alkane groups. The alkane and carboxylic groups specified by different bands are arise from titanium tetra isopropoxide and 2-propanol (precursor material), when we used in the synthesis process. In addition, a broad absorption band between 500 and 1,000 cm<sup>-1</sup> is ascribed to the vibration absorption of the Ti–O–Ti linkages in TiO<sub>2</sub> nanoparticles (Lu et al. 2008).

Ultra violet-diffuse reflectance spectra (UV-DRS)

The optical properties of samples were characterized by UV-DRS. The diffused reflectance spectra of undoped and



different weight percentages (4, 8, 12 and 16 %) of Codoped  $TiO_2$  are shown in (Fig. 3).

In anatase phase of  $TiO_2$ ,  $Ti^{4+}$  is surrounded by six oxygen atoms in an octahedral coordination, forming  $TiO_6$ octahedra. When Co<sup>2+</sup> substitutes Ti<sup>4+</sup>, it forms bond with six oxygen atoms. Now, according to crystal field theory, the electrons in the d-orbital of Co<sup>2+</sup> will undergo repulsion by the electrons of the six surrounding oxygen atoms. This results in the splitting of d-orbital of  $Co^{2+}$ , showing the aforementioned d-d transition. These types of electronic transition will be by  $Co^{2+}$  when it substitutes  $Ti^{4+}$ and remains in octahedral or pseudo octahedral coordination (Choudhury and Choudhury 2012). The DRS spectrum of TiO<sub>2</sub> showed a broad intense absorption at around 345 nm due to the charge transfer from the valence band formed by 2p orbitals of the oxide anions to the conduction band formed by 3d  $t_{2\sigma}$  orbitals of the Ti <sup>4+</sup> cations (Sadanandam et al. 2013; Kirit and Dimple 2012).

From the UV–VIS DRS spectra (Fig. 3), bare TiO<sub>2</sub> particles exhibit strong absorption at  $\lambda < 400$  nm. Compared to the spectrum of bare TiO<sub>2</sub>, there is a new absorption band present between 400 and 800 nm of all samples, which means band gap absorption onset was extended into the visible light region for all Co-doped TiO<sub>2</sub> samples. The absorption bands at 200–400 nm are due to the charge transfer from the valence band to the conduction band of TiO<sub>2</sub>.

However, on 12 %  $\text{Co}^{2+}$  doping, the absorption spectrum is positioned at 748 nm. At 16 % of doping, the absorption peak is blue shifted to 742 nm. On increasing the concentration of doping, the value of blue shift increases with the enhancement in the intensity of visible band. The band gap energies were calculated from the cut-off wavelength of bare and Co-doped TiO<sub>2</sub> using the Eq. (2).

$$E_{\rm g} = \frac{hc}{\lambda} \,\mathrm{eV}; \ E_{\rm g} = \frac{1,240}{\lambda} \,\mathrm{eV}$$
 (2)

where  $E_{\rm g}$  is the band gap energy (eV), *h* is the Planck's constant (6.626 × 10<sup>-34</sup> Js), *c* is the light velocity (3 × 108 m/s), and  $\lambda$  is the wavelength (nm).

The calculated values are 3.58 eV (345 nm), 3.65 eV (339 nm), 3.75 eV (330 nm), 3.81 eV (325 nm), and 3.93 eV (315 nm) for bare TiO<sub>2</sub> and TiO<sub>2</sub> doped with 4, 8, 12, and 16 wt% of Co<sup>2+</sup>, respectively, and are given in (Table 2).

Table 2 Band gap energy for bare and Co-doped TiO2 nanoparticle

Samples	Band gap (eV)		
Bare TiO <sub>2</sub>	3.58		
4 % Co-doped TiO <sub>2</sub>	3.65		
8 % Co-doped TiO <sub>2</sub>	3.75		
12 % Co-doped TiO <sub>2</sub>	3.81		
16 % Co-doped TiO <sub>2</sub>	3.93		

From the Table 2, it is noted that bare  $TiO_2$  nanoparticle has a larger band gap (3.58 eV) than that of bulk  $TiO_2$ nanomaterial (3.2 eV), which is quite expected due to quantum confinement effect. But, after various levels of cobalt doping, the band gap is running between 3.65 and 3.93 eV.

#### Photoluminescence (PL)

PL emission spectra of bare and 16 wt% of Co-doped TiO<sub>2</sub> with 300 nm excitation are shown in (Fig. 4). The PL spectrum of TiO<sub>2</sub> exhibits a UV emission (373 nm) and two visible emissions: one at 431 nm and the other at 587 nm. The UV emission is considered as the band edge emission of the host TiO<sub>2</sub>, and the 431 nm peak can be ascribed to self-trapped excitations localized in TiO<sub>6</sub> octahedra (Wan et al. 2010). The existences of green emission peak at 587 nm explain the presence of oxygen vacancies (Abazovic et al. 2006). When compared with bare TiO<sub>2</sub>, the PL emission bands of doped product are blue shifted with intensity reduction in the UV band and enhancement in the visible bands (Kirit and Dimple 2012).

Scanning electron microscope (SEM with EDX)

Figures 5 and 6 show typical scanning electron microscopic images of bare and 16 wt% Co-doped TiO<sub>2</sub> nanoparticle. From the figures, the most of the particles are almost spherical in shape with uniform size distribution (Reddy et al. 2010). It is evident that the growth of particle is restrained by Co on doping with TiO<sub>2</sub>. A closer examination of these figures reveals a well-defined particle like morphology, having abundance of spherical-shaped particles, with the average agglomerated particle size in the range of 15.31-25.92 nm. The spherical shape is



Fig. 4 PL spectra for bare TiO<sub>2</sub> and Co-doped TiO<sub>2</sub> nanoparticle

**Fig. 5** SEM micrograph of TiO<sub>2</sub> nanoparticles (**a**, **b**) and corresponding to EDX diagram (**c**)





significantly important not only for the design of surface properties and surface area, but also for tuning the electronic structure i.e., to make the visible light spectrum more active for the better photocatalytic activity (Narayana et al. 2011). Energy-dispersive X-ray spectroscopy (EDAX) of 16 wt% of Co-doped TiO<sub>2</sub> (Figs. 5c, 6c) shows the presence of O, Ti and cobalt according to atomic weight stoichiometric of 74.71, 24.05 and 1.24 %, respectively (Kirit and Dimple 2012).







Transmission electron microscope (TEM)

Figures 7a, b and 8a, b illustrate the transmission electron microscope (TEM) images of the bare and 16 wt% Codoped TiO<sub>2</sub> nanoparticles obtained after 500 °C of annealing. They showed almost spherical shape particles with uniform size distribution. As can be seen from the TEM image that the particle sizes are in the range of 15-25 nm, which is in good agreement with the crystallite size obtained from XRD results. In general, TiO<sub>2</sub> nanoparticles appear in transparent spherical shape. On incorporation of cobalt particles dark patches are seen on the surface of transparent TiO<sub>2</sub> nanoparticles. Electron diffraction patterns showed the brightness and intensity of polymorphic discrete ring of the highly crystalline nanoparticles are shown in (Figs. 7c and 8c).

Non-linear optical studies

For the preparation of NLO study, the oven-dried powders of bare  $TiO_2$  and 16 wt% Co-doped  $TiO_2$  were kept into



muffle furnace and annealed at 800 °C for 5 h to obtain the rutile phase. The study of non-linear optical conversion efficiency was carried out using the experiment setup of Kurtz and Perry. A Q-switched Nd-YAG laser beam of wavelength 1,064 nm, with a repetition rate of 10 Hz was used. The bare TiO2 and Co-doped TiO2 were nanopowdered with a uniform particle size and then packed in a microcapillary of uniform bore and exposed to laser radiations. The SHG was confirmed by the emission of green radiation of 532 nm wavelengths and the parent ray was filtered using IR filter. A sample of potassium di hydrogen phosphate (KDP) also powdered to the same particle size as the experimental sample was used as a reference material in the present measurement. The relative SHG measurement gave conversion efficiency of bare  $TiO_2$ . Thus, the efficiency shows an output of 8.0 mV for bare TiO<sub>2</sub>, 6.0 mV for Co-doped TiO<sub>2</sub> and 10.2 mV for KDP. When compared to 10.2 mV of KDP, for same input laser power, the bare and Co-doped TiO<sub>2</sub> show lesser second harmonic efficiencies. The calculated results are represented in Table 3.

Fig. 8 TEM image of Co-doped TiO<sub>2</sub> nanoparticles (a, b) and corresponding to SAED pattern (c)



Table 3 Comparision of SHG efficiency of bare and 16 % Co-doped TiO\_2 nanoparticles

Samples	Input (mJ/pulse)	Output (mV)	KDP (mV)	SHG efficiency
Bare TiO <sub>2</sub>	4.5	8.0	10.2	0.78
Co-doped TiO <sub>2</sub>	4.5	6.0	10.2	0.58

# Conclusion

We have successfully synthesized the bare and different weight percentages (4, 8, 12 and 16 %) of Co-doped TiO<sub>2</sub> nanoparticles by means of sol–gel method at room temperature. The synthesized products were annealed at 500 and 800 °C for getting anatase and rutile phases, respectively. The annealed samples were characterized by the techniques like XRD, FTIR, and UV-DRS. The doping concentration of 16 wt% was chosen for further analysis like PL, SEM with EDX, TEM with SAED pattern, and NLO. From the results of XRD patterns, it is confirmed that the TiO<sub>2</sub> was in anatase phase with crystallite sizes in the range of 15.31-25.92 nm. In comparison with undoped TiO<sub>2</sub>, all the doped products show increased particle size. The existences of functional groups were identified by FTIR analysis. The cut-off wavelengths were identified by UV–VIS DRS analysis and the band gap energies of the undoped and doped products are having values between 3.58 and 3.93 eV. The PL emission spectra show the creation of new luminescent centers. The SEM with EDX and TEM image with SAED pattern confirm the spherical morphology of the products. In SHG, bare TiO<sub>2</sub> shows greater NLO efficiency than the doped product.

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