The investigation on structural, optical and morphological behavior of pure and co-doped TiO₂ nanoparticles developed via sol-gel approach for biological activity

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Abstract

In the present work, the effect of pure and different weight % of Cobalt (Co) doped titanium dioxide (TiO₂) nanoparticles (NPs) were developed from sol–gel approach. The powder x-ray diffraction pattern of pure and 1%, 3%, and 5% Co-doped TiO₂ NPs confirms the anatase phase structure and average crystallite size was obtained from 37, 38, 42 and 48 nm respectively for pure TiO₂ and 1%, 3%, and 5% Co-doped TiO₂. The spherical-like morphology was observed from the prepared materials which were primarily confirmed by the FESEM analysis. The optical behaviour of the developed material was investigated by UV–vis spectrum and energy band gap was achieved to be 1.95 eV, 3.96 eV, 3.89 eV and 3.62 eV respectively for pure TiO₂, 1 wt%, 3 wt% and 5 wt% Co-doped TiO₂ NP. The Kirby Bauer Agar Well Diffusion Assay method was employed to explore antimicrobial activity of nanosized pure and Co-doped TiO₂ colloidal suspension against the test microorganisms two Gram positive bacteria (Staphylococcus aureus, Bacillus subtilis), two Gram negative Bacteria (Escherichia coli, Pseudomonas aeruginosa), and two fungi (Candida albicans, Aspergillus niger). It shows that the Co-doped TiO₂ NPs inhibited the multiplication and growth of the above mentioned test bacteria and fungi. Antimicrobial activity was found against all tested microorganisms and confirmed that Co-doped TiO₂ NPs possess higher antimicrobial activity at various concentration range of 25 μg, 50 μg, 75 μg and100 μg respectively for 1 wt%, 3 wt% and 5 wt% Co-doped TiO₂ solutions.

1. Introduction

In recent trends, Titanium dioxide (TiO₂) nanoparticles (NPs) play a drastic role in environmental purification owing to its photo induced super-hydrophobicity, nontoxicity and antifogging effect [1]. These types of properties have been widely used for eradicating bacteria and harmful organic materials from water and air. It is also used in self-cleaning and self sterilizing surfaces for places in medical centers. The performance of TiO₂ NPs strongly depends on size, crystalline structure and morphology of the particles [1]. So, there has been a variety of researchers focusing on the preparation of nanoparticles of TiO₂ using ethanol along with different acids and bases for various applications such as photo catalytic, photoconductors, solar cells, gas sensors due to their light absorption, high refractive index, non-toxic property, high chemical stability and low-cost of production [2, 3]. There are several methods are available to prepare TiO₂ NPs such as ion-impregnation, sol–gel precipitation, hydrothermal and sol–gel approach [4]. Among them, sol–gel approach is sophisticated method to prepare particles [5]. In addition, sol–gel technique is one of the well-suited synthetic approach for prepare novel metal oxide semiconductor nanoparticles due to their less chemical usage, low-temperature treatment and no requirement for special equipment [5, 6]. Also this technique is used to control the particle size at low temperature [6].
In current decade, antibacterial agents are more attracted in several industries like food disinfection, hospital implants and medicine [7]. Owing to this reason, researchers are paying attention to examine the antimicrobial property of transition metals (Tungsten, Manganese, Nickel, Copper, Cobalt etc) doped titanium dioxide used for prevent and control the dispersal of bacterial infections [4, 8]. Because, transition metal doped with metal oxide nanoparticles has higher biological activity due to its rapid recombination of photoactivated electrons and positive holes which generating Reactive Oxygen Species (ROS) [7, 8]. Hence, antimicrobial activities of TiO₂ mixed ligand have been studied to possess considerable antibacterial activity [9, 10].

To overcome the environmental problems in our present study focused to develop pure and Co doped TiO₂ NPs from sol-gel approach for antimicrobial activity. In addition, the as prepared samples were analysed their structural, morphological and optical properties at the nanoscale. The attained particle size acts a vital role in the optical and anti-microbial properties.

2. Materials and methods

2.1. Analytical instrumentation

The Powder x-ray diffraction pattern of pure and Co doped TiO₂ NPs were taken by the model of Lab X XRD6000 Shimadzu. The morphological studies of High Resolution Scanning Electron Microscope were investigated from the instrument of FEI Quanta FEG 200. The absorption spectra and optical band gap of the TiO₂ and Co doped TiO₂ NPs samples were determined by the instrument of UV–vis spectrophotometer (JASCO U-670 Spectrometer). A PL spectrum was recorded between 370 and 770 nm and it was taken by the instrument of Horiba Jobynvon model spectrophotometer. FTIR absorption spectrum was recorded by JASCOFP8200 spectrophotometer. The individual shape and size of the particle was revealed by using High Resolution Transmission Electron Microscope JE2100 (JEOL–200 KV, LB6 filament) and EDAX analysis was used to find out the composition of pure and doped TiO₂ NPs samples by using the detector attached with the same instrument.

2.2. Materials for synthesis of Co doped TiO₂ NPs

Titanium isoproxideoxide (Ti{OCH(CH₃)₂})₄(Sigma-Aldrich >97% pure) and cobaltous sulphate heptahydrate (CoSO₄·7(H₂O)₂)(Merck >99% pure) were used as precursor material. The ethanol (C₂H₅OH) (Hayman (German) 99.99%), hydroxylamine hydrochloride (NH₂OH·HCl)(Sigma-Aldrich 99%) and Double distilled (DD) water is used for over all preparation of NPs. Bacterial cultures such as Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa, and fungus cultures such as Candida albicans, Aspergillus niger were obtained from Eumic Analytical Lab and Research Institute, Tiruchirappalli. Bacterial strains were maintained on nutrient agar slants (Hi media) at 4 °C.

2.3. Synthesis of Co-doped TiO₂ NPs

For the preparation of 1 wt%, 3 wt%, 5 wt% Co-doped TiO₂ NPs, aqueous solution of Ti{OCH(CH₃)₂}₄ used as a starting precursor material. At room temperature, sol was prepared by 1:8 molar ratio of mixing Ti{OCH(CH₃)₂}₄(2.6 ml) with 24 ml of C₂H₅OH and dissolved 1000 ml of DD water. 0.694 g of NH₂OH·HCl was added into 100 ml of DD water and added slowly to the above prepared Ti{OCH(CH₃)₂}₄ sol. For cobalt doping, 1 wt% of CoSO₄·7(H₂O)₇ solution was mixed with TiO₂ sol. Then, the mixture of Ti{OCH(CH₃)₂}₄ and CoSO₄·7(H₂O)₇ solutions were stirred for 3 h in a magnetic stirred and centrifuged at 15 min. After centrifugation, obtained precipitate was dried (80 °C) at oven and subsequently annealed at 600 °C for 5 h in a muffle furnace. Similarly, 3 wt% and 5 wt% Co-doped TiO₂ NPs were prepared as mentioned in the above synthesis method.

2.4. Preparation of culture media

The nutrient agar medium was developed and sterilized by autoclaving at 121 °C 15 lbs pressure for 15 min then aseptically poured the medium into the sterile petriplates and allowed to solidify the bacterial and fungal broth culture was swabbed on each petriplates using sterile buds. Then, wells were made by well cutter. 1, 3 and 5 wt% Co-doped TiO₂ NPs containing solutions were prepared dissolving 100 mg of each in 100 ml of DMSO solvent and from this stock solution, different concentrations (25 μg, 50 μg, 75 μg and 100 μg) of 1, 3 and 5 wt% Co-doped TiO₂ NPs calculated at 600 °C solutions were taken for assay. The antimicrobial activity of pure TiO₂, 1, 3 and 5 wt% of Co-doped TiO₂ NPs were assayed against Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa, Aspergillus nigerand Candida albicans at 37 °C for 24 h. After incubation, the plates were observed for the zone of inhibition. The bacterial and fungal viable count was determined after 24 h by plating 1, 3 and 5 wt% Co-doped TiO₂ NPs on nutrient agar plates and the number of colony forming units (CFU) were counted by a viable count method. To control this, the bacterial and fungal cultures were incubated
with Gentamicin. The sample material which has antimicrobial activity was identified by inhibited growth of the microorganisms and it was clearly seen as distinct zone of inhibition. The diameter of zone of inhibition was measured and expressed in millimetre.

3. Result and discussion

3.1. Powder x-ray diffraction (PXRD) studies

The PXRD analysis was primarily identified crystalline phase structure of the synthesized NPs. The PXRD pattern reveals all intensity peaks are corresponding to the crystal planes of (101), (004), (200), (105), (211), (204), (116), (220) and (215), respectively for pure and cobalt doped TiO₂ NPs [11]. This indicates the formation of anatase phase of titanium dioxide NPs [JCPDS Card No 89-4921] belonging to the tetragonal structure [11]. All the peaks present in the PXRD pattern of Co-doped TiO₂ NPs shows the characteristics diffraction peaks of anatase phase which is similar to XRD pattern of pure TiO₂ NPs. The intensity peak (101) linearly increases with increasing of Co-dopants with TiO₂ due to the ionic radius of Co²⁺ (0.65 Å) which are higher to that of Ti⁴⁺ (0.61 Å) ionic radius. So, Co²⁺ easily occupy Ti⁴⁺ sites within TiO₂ crystal lattice structure [12]. And also, the (101) peak was shifted towards higher angle side by adding the Co-dopants with TiO₂ due to Co-ions are perfectly incorporated into the TiO₂ lattice. This report is well matched with the previous report [12, 13]. So, Ti⁴⁺ ions can be easily replaced by Co²⁺ ions which were revealed in figure 2. The average particle size was calculated by using the Debye–Scherrer’s formula.

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

Where, D is the size of particles, \( \lambda \) is the wavelength of the x-ray beam, \( \beta \) is Full Width Half Maximum (FWHM) of the peak, \( \theta \) is diffraction angle and K is shaping factor [14, 15]. The particle average size of pure, 1 wt%, 3 wt% and 5 wt% Co-TiO₂ NPs are about 37 nm, 38 nm, 42 nm and 48 nm, respectively. The defects induced in the prepared materials were find out by dislocation density (\( \delta \)) and calculated by using equation.

\[ \delta = \frac{1}{D^2} \]

Where, D represents the crystallite size. The dislocation density (\( \delta \)) was found to be 14.54 × 10⁻³ nm⁻², 14.23 × 10⁻³ nm⁻², 11.22 × 10⁻³ nm⁻² and 10.94 × 10⁻³ nm⁻² respectively for 1 wt%, 3 wt% and 5 wt% Co-TiO₂ NPs [14, 16].

3.2. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectrum of pure TiO₂ NPs and 1 wt%, 3 wt%, 5 wt% Co-doped TiO₂ NPs were shown in the figure 3. The two peaks around at 3420 cm⁻¹ and 1585 cm⁻¹ are corresponds to O–H stretching and H–O–H bending vibrations which originates from the water content presence in the synthesized materials [11]. A band at
2354 cm$^{-1}$ is ascribed to the presence of CO$_2$ in air medium [11]. The bands at 478 and 651 cm$^{-1}$ are attributed by the metal oxide modes of Ti–O–Ti and Co–O–Ti [17]. In addition, the absorption of Co-doped peaks shifts towards the higher wave number side than the pure TiO$_2$, which is clearly representing the change in the bond length by the substitution (or) replacement of Co ion instead of Ti ion [18]. From the observed FT-IR spectra, there is no additional band observed which representing there is no additional chemical bonding presence in between of Co-doped TiO$_2$ and pure TiO$_2$.

3.3. UV–visible spectroscopy

The UV-Visible spectroscopy helps to understand the optical properties and bandgap of the prepared NPs. The UV-Visible spectra of pure TiO$_2$ NPs, 1%, 3% and 5 wt% Co-doped TiO$_2$ NPs were shown in the figure 4. It was recorded in the range of 200 nm to 800 nm. The UV-Visible spectrum of pure TiO$_2$ NPs obtained at 350 nm attribute to charge-transfer from the valence band formed by 2p orbitals of the oxide anions to the conduction band formed by the 3d orbitals of the Ti$^{4+}$ cations [19]. The absorption was shift towards the lower wavelength side for pure TiO$_2$ NPs compared with Co-doped TiO$_2$ NPs due to blue shift in absorbance. But in the case of UV-Vis absorbance spectra of doped TiO$_2$ NPs, 1 wt% Co-doped TiO$_2$ NPs compared with other 3 wt% and 5 wt% Co-doped TiO$_2$ NPs observed red shift. It can also be seen that from the figure 4 optical absorption edges were shifted to higher wavelength region (red shift) with increasing dopant cobalt. This shift may occur due to Co successfully incorporate with TiO$_2$. The Energy band gap was primarily estimated from the prepared material by using tauc’s relation [20].
Where, $\alpha$, $h\nu$ and $A$ is absorption coefficient, photon energy and band tailing parameter. The optical bandgap ($E_g$) is attained to be 1.95 eV, 3.96 eV, 3.89 eV and 3.62 eV respectively for pure TiO$_2$, 1%, 3% and 5% Co-doped TiO$_2$ NPs (figure 5). From the band gap values of Co-doped TiO$_2$ NPs decreases when increase in the doping of cobalt content. The two mechanism may be responsible for the narrowing the band gap. The first one is new d-states are introduced near the valence band edge which narrow the band gap of the TiO$_2$ system and the second was substitution of dopant Co$^{2+}$ to the Ti$^{4+}$ site introduced defect states related by oxygen vacancy in the forbidden energy band gap zone of TiO$_2$ NPs [21].

### 3.4. Photoluminescence (PL) spectroscopy

PL spectrum is an important tool to identifying the efficiency of trapping of charge carrier, transfer and circumstances of electron-hole pairs in semiconductor particles. The figure 5 shows the excitation wavelength of the pure TiO$_2$ NPs and Co-doped TiO$_2$ NPs is found between 300 nm and 400 nm. The excitation wavelength observed for pure TiO$_2$ nanoparticle was 316 nm respectively for Near Band Edge (NBE) emission [22]. Similarly, for other excitation wavelength of Co-doped TiO$_2$ NPs was observed at 307 nm, 325 nm, 339 nm and 352 which indicates that trapped electrons and oxygen vacancies [22]. In the presence of light irradiation, PL emission intensity of pure TiO$_2$ NPs is decreases with increasing Co (1 wt%, 3 wt% and 5 wt%) dopant which may creates owing to lesser recombination rate of electrons and holes by their cobalt ion successfully incorporate into TiO$_2$ [23].
3.5. Field emission scanning electron microscopy (FESEM)

The figures 7(a)–(d) shows FESEM images of pure TiO$_2$ NPs and 1%, 3% and 5% of Co-doped TiO$_2$ NPs. The FESEM images of the cobalt doped TiO$_2$ NPs shows most of the NPs are almost uniform and spherical sized particles, coherent together and also closer view shows that spherical particle. These spherical shaped particles size in the range of 38 nm to 42 nm. The EDAX analysis is an important tool to determine the chemical composition of synthesized material. Figures 8(a) and (b) depicts EDAX spectrum of pure and 5 wt% Co-doped TiO$_2$ NPs which reveals no more than elements of titanium, cobalt and oxygen presence in the synthesized material and free from any noticeable impurities in the material.
3.6. High resolution transmission electron microscopy (HRTEM)

The high resolution transmission electron microscopy is an important tool to measure the distribution of the

crystallites, actual size, etc. The HRTEM images of 5% of Co-doped TiO₂ NPs are shown in the

figure 9. The synthesized NPs 5% of Co-doped TiO₂ present in the image were in the range of nano scale size. It was also
clearly confirmed from the image that, the individual NPs were seen and each of these smaller single particles
agglomerated to form large particle. The particle size of 5% Co-doped TiO₂ NPs is achieved to be 20–50 nm. The

figure (b) exhibit lattice fringes were used to calculate the d-spacing and it was found 2.89 nm. The calculated
d-spacing value was compared with standard JCPDS data. It was found that the d-spacing corresponding to the

hkl plane (215) of anatase TiO₂ NPs.

3.7. Antimicrobial activity of Co-doped TiO₂ NPs

The antimicrobial activities of the samples were identified from the zone of inhibition. Figure 10 shows the

antimicrobial activity variation of various pathogens which were exposed to 25, 50, 75 and 100 μg ml⁻¹

concentration of pure and Co-doped TiO₂ NPs. The diameter of zone of inhibition was measured and expressed

in millimetre. The results showed for all the four samples at different concentration showed some zone of

inhibition against all the pathogens used. In addition, it could be observed that the doped samples were having

higher zone of inhibition than the pure TiO₂ NPs. It shows that there was a significant effect of the cobalt

induced antimicrobial activity for the doped nanoparticle samples. Also, the zone of inhibition increases as the

concentration of the samples increases for almost all the samples against all the pathogens. However, none of the

samples were able to reach the zone of inhibition of the standard Gentamicin except for the two samples which

showed some higher zone of inhibition against the gram positive bacteria. The proposed possible antimicrobial

mechanism of TiO₂ is the generation of intracellular Reactive Oxygen Species (ROS) from the surfaces of the

nanoparticles of TiO₂. This ROS directly attack the microbial membrane and enter in to the microbial cell,
oxidation of intracellular coenzyme A, damage the DNA and peroxidation of large number of lipids and decrease
the respiratory activity which leads cell death [24]. The 1 wt% Co-doped TiO₂ NPs at higher concentration

Figure 8. EDAX spectrum of (a) pure TiO₂ and (b) 5 wt% Co-doped TiO₂ NPs.

Figure 9. Different magnification HRTEM images of (a) and (b) 5 wt% Co-doped TiO₂ NPs.

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Figure 10. Inhibition zone of different microorganisms by media subjected to pure and Co-doped TiO$_2$ nanoparticles calcinated at 600 °C.
(100 μg) showed a higher zone of inhibition against the gram positive bacteria *Staphylococcus aureus* compared to other pure and doped samples including the standard Gentamicin. Similar results were observed for the 3 wt% Co-doped TiO2 NPs against the gram positive bacteria *Bacillus subtilis* (figure 11). The samples (5 wt% Co-doped TiO2 NPs) at higher concentrations reach the standard Gentamicin in terms of the zone of inhibition against the gram negative bacteria *Escherichia coli* and *Pseudomonas aeruginosa*. These results proved that the effect of the Co doping on TiO2 NPs enhanced the antimicrobial activity due to modified surface area and morphology.

Figure 11. Antimicrobial effect of pure and Co-doped TiO2 nanoparticles calcinated at 600 °C.
4. Conclusion
The pure and 1%, 3% and 5% Co-doped TiO₂ NPs were successfully achieved from sol–gel approach for biological application. The average particle size of the pure and 1%, 3% and 5% Co-doped TiO₂ NPs were determined by Debye–Scherrer’s formula is 37 nm, 38 nm, 42 nm and 48 nm. FESEM images shows uniform spherical sized particles were observed in the prepared material. The EDAX analysis depicts no other impurities are attained in the prepared pure and Co-doped TiO₂ NPs. In UV–vis spectrum, energy band gap of the pure TiO₂ NPs increases with adding dopant of 1 wt%, 3% and 5% Co-doped TiO₂ NPs which may occur due to Co successfully incorporate with TiO₂. In photoluminescence spectra, the PL emission between 300 nm to 400 nm corresponds to the NBE emission which creates due to the direct recombination between electrons in the conduction band and holes in the valence band. High resolution transmission electron microscopy of Co doped TiO₂ nanoparticles shows particles are looks like spherical in shape approximately uniform size of 20 to 50 nm. FTIR spectrum analysis shows the peaks from 478 cm⁻¹ and 651 cm⁻¹ bending and stretching mode of Ti–O–Ti and Co–O–Ti. Studies an antimicrobial activity of Co doped TiO₂ shows that the highest antimicrobial activity compared to pure samples due to ROS create the hydrogen peroxide (H₂O₂), superoxide free radical (O₂⁻) and hydroxyl free radical (OH %) in the cell wall membrane which is increasing the antimicrobial activity by increasing the dopant concentration.

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