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Surfactant assisted synthesis of cobalt doped titania nanomaterial: Characterization and its applications in photocatalysis and anti-bacterial activity

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The synthesis of 0.5 wt. % cobalt doped titania nanomaterial (Co^{2+}-TiO_2) assisted by sodium dodecyl sulfate anionic surfactant by sol-gel method is reported. The synthesized catalysts are characterized by XRD, UV-vis DRS, FT-IR, BET, TEM, SEM and XPS analysis. XRD results show that all the catalysts are in anatase phase. UV-vis DRS studies indicate that decrease in band gap of TiO_2 is due to doping of Co^{2+}. FT-IR studies indicate the insertion of Co^{2+} into TiO_2 lattice as a substitutional dopant. BET analysis shows an increase in surface area of the catalyst. From SEM and TEM analysis, change in the morphology of the particles with reduced particle size is observed. XPS studies confirm the presence of Co^{2+} along with Ti and O. The photocatalytic efficiency of the catalyst has been evaluated by degradation of methyl red under visible light irradiation at various reaction parameters. The antibacterial activity of the catalyst against *Escherichia coli* has also been investigated.

Keywords: Cobalt doped titania, Titania, Nanomaterials, Surfactants, Dye degradation, Sol-gel method, Antibacterial activity, Methyl red,

Water sources polluted by textile industries contain high percent of large amounts of azo dyes, which owing to their non-biodegradability, toxicity and potential carcinogenic nature constitute a major threat to the surrounding ecosystem[1, 2]. Similarly the presence of microorganisms namely bacteria, fungi etc. deteriorate water quality and cause many pathogenic diseases. Methyl red, an azo dye was widely used in textile dyeing, paper and printing industries and causes high toxic effects[3]. Therefore, it is necessary to disinfect the polluted waters and much attention has been focused to synthesize a catalyst which is environmental friendly, cost-effective and can degrade the dyes as well as can act as safe antibacterial agents. Heterogeneous photocatalysis was found to be an efficient method for removal of such dyes from industrial wastewaters. Titania has been selected as the best photocatalyst for this process as it was nontoxic, stable with respect to photochemical corrosion and insoluble under any drastic conditions[4]. It can be used in environmental biodecontamination for a large variety of organisms like bacteria, viruses etc along with degradation of azo dyes and convert them to CO_2, H_2O and harmless inorganic anions[5]. However, some of its disadvantages include high band gap energy of TiO_2 (E_{bg} = 3.2 eV) and the high rate of electron hole recombination within nanoseconds, at TiO_2 particles. In order to rectify these defects and to exhibit high reactivity under visible light ($\lambda > 400$ nm), doping of titania with metals[6] and nonmetals[7-10] were preferred. There were very few reports regarding cobalt doped titania by different methods in the literature[11] and no one has reported on synthesis of Co^{2+}-TiO_2 assisted by anionic surfactant: Sodium dodecyl sulfate surfactant so far. Doping of cobalt into titania was preferred, since it acts as an electron trap leading to decrease in the band gap energy. Surfactants were the most promising in practical application areas like synthesis of nanoparticles[12, 13]. Though surfactant medium plays a vital role in the synthesis of a variety of nanoparticles, the photocatalytic efficiency of such titania samples depends on the template selected[14-16]. The main aim of the present work was to synthesize Co^{2+}-TiO_2 nano material and to investigate the effect of surfactant on the size, morphology, specific surface area of the nanocatalyst. We have adopted sol gel method since it was more advantageous and economical for synthesis. Investigations were carried out on its applications towards enhancement in photocatalytic and antibacterial activity in visible light. The commonly existing bacteria in effluent water, *Escherichia coli*. (*E. coli*, Gram-negative bacteria) species was selected as model organism for the study of antibacterial activity of the as prepared catalyst.

Materials and Methods

Titanium tetra-*n*-butoxide [$Ti(O\text{-}Bu)_4$], cobalt nitrate obtained from E. Merck (Germany), were used as titanium, cobalt sources for preparing Undoped TiO_2 and cobalt doped TiO_2 photocatalysts. Super-dry purified ethanol has been used. Sodium dodecyl sulfate was used as surfactant medium and obtained from Sigma-Aldrich. Methyl red was used as a model pollutant (India, analytical grade) for degradation studies. *E. coli* (ATCC 8739) was used for investigation of the catalyst towards antibacterial activity studies. All the other chemicals and reagents were of Merck (India) analytical grade. Furnace with maximum temperature limit of 1200 °C of V B Ceramics India Ltd, have been used for the calcinations purpose.

The XRD patterns were recorded with a Bruker AXS D8 advance diffractometer at room temperature with Cu-Kα of wavelength (λ) 1.5406 Å, and carbon monochromator. The diffractograms were recorded in the range of 10-80 °C. The accelerating voltage of 35 kV and emission current of 30 mA were employed. The UV-visible absorption spectroscopic analysis of the catalysts was done by using a UV-vis-NIR spectrophotometer (Varian, Cary 5000). X-ray photo electron spectroscopy (XPS) of the prepared catalysts were recorded with auger electron spectroscopy (AES) module PHI 5000 Versa Prob II, FEI Inc. using the Al-Kα line of a 100 W X-ray tube as a radiation source with the energy of 1253.6 eV, 16 mA × 23.5 kV and a working pressure lower than 1×10^{-8} Nm^{-2}. Scanning electron micrographs (SEM) of the samples were recorded using JEOL (model JSM 6390LV). Infrared spectra of the synthesized samples were recorded on Thermo Nicolet Nexus 670 spectrometer, with resolution of 4 cm^{-1} in KBr pellets. For understanding the particle size of the catalysts TEM measurements were made using JEOL/JEM 2100 instrument, operated at 200 kV. In this study, the Brunauer-Emmett-Teller (BET) surface area was determined from the N_2 adsorption-desorption isotherm at 77.3 K by using an Autosorb I Quantachrome Corp. system.

Synthesis of cobalt doped TiO_2 by surfactant assisted sol-gel method

For the synthesis of 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) titanium tetrabutoxide was taken a titanium precursor and cobalt nitrate was taken as source for dopant. Sodium dodecyl sulfate was used as surfactant medium. Initially, solution I was prepared by taking 21.0 mL of titanium tetra-butoxide in 40.0 mL of absolute alcohol with stirring for 10 minutes and then 3.0 mL of nitric acid was added drop wise under continuous stirring for 30 minutes. Solution II contained 40.0 mL of absolute ethanol (100%) and 0.01475 g of cobalt nitrate dissolved in 7.1 mL of water. To this 25 mL of 0.05 M SDS surfactant solution was added and stirred vigorously for 30 min. Solution II was added slowly to the solution I and stirred continuously. The pH was maintained at around 8 by adding ammonium hydroxide. Vigorous stirring was continued at room temperature until the transparent sol was obtained. The resulting sol was stirred for 2 h and then aged at 25 °C for 48 h. The gel was dried at 110 °C in an oven for 12 h. The catalyst 0.5 wt.% Co^{2+}/TiO_2-(catalyst prepared in presence of SDS surfactant) was calcined at 450 °C in a furnace for 4 h. A cobalt doped TiO_2 sample without surfactant was also prepared by adopting the same procedure but without surfactant medium and is referred to as Co^{2+}-TiO_2. cobalt doped titania catalysts of various compositions, 0.25, 0.5, 0.75 and 1.0 wt.%, were synthesized. The powders were stored in black coated air-tight glass containers and were used for XRD analysis, UV-visible absorption studies, XPS, SEM, TEM, BET and FT-IR studies and for photocatalytic activity testing. We have carried out trial photocatalytic degradation reactions and higher activity was found with the present 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant). Hence, characterizations were carried on with undoped TiO_2 labeled as (C-1), 0.5 wt.% Co^{2+}/TiO_2 labeled as (C-2) and 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant), labeled as (C-3).

Photocatalytic activity studies

The photocatalytic activity of the catalyst C-3 was estimated by carrying out the photocatalytic degradation of methyl red dye in the presence of visible light in the photo catalytic reactor. The photocatalytic degradation was carried out with 100 mL of aqueous methyl red dye solution of required concentration (1-10 mg L^{-1}) containing 100 mg of the catalyst considered in 150 mL of Pyrex glass vessel under continuous stirring. The mixture was stirred for 45 min in the dark in order to attain adsorption-desorption equilibrium of methyl red dye on the catalyst surface. The pH of the solution was maintained by adding 0.1 *M* HCl and 0.1 *M* NaOH. The mixture was placed inside the photocatalytic reactor where the distance between the light and the reaction vessel was 20 cm away from the visible light source. It was irradiated under visible light (wavelength range 400–800 nm) using a UV filtered Osram high pressure mercury vapour lamp with power 400W and 35000 lum. The description regarding the photocatalytic set up is given elsewhere[17]. Cut-off filters oriel (51472) was placed in the path of the light for the complete removal of UV radiation. Running water was circulated around the sample container in order to filter IR radiation and to maintain the reaction mixture at the room temperature. At regular time intervals, 5 mL of the aliquots were taken from the solution and centrifuged and the absorbance was measured where λ_{max} for methyl red 525 nm by using Milton Roy Spectronic 1201, UV-vis spectrophotometer. The percentage degradation of the methyl red was calculated by using a calibrated relationship between the measured absorbance and its concentration (%) as $(A_0–A_t)/ A_0\times100$, where A_0 = initial absorbance of methyl red dye solution, A_t = absorbance of methyl red dye solution at time *t*.

Antibacterial activity

In the agar diffusion method for the preparation of nutrient agar medium: 15.0 g agar, 5.0 g of peptone, 3.0 g of beef extract and 5.0 g of sodium chloride were dissolved in 1000 mL distilled water and the pH was adjusted to 7.0. The obtained agar medium was sterilized at 121 °C at pressure of 15 lb for 20 min. The prepared nutrient broth was cultured in an incubator at 37 °C for 2 days. Required amount of the C-3 photocatalyst was added to 9 mL of 0.9 % saline solution and it was sterilized by autoclaving at 120 and 15 lbs for 20 min. Initially 20 mL of nutrient agar was poured in sterilized petridishes. 0.5 mL of active bacterial culture was homogenously spread on these agar plates. All these petridishes were incubated for 24 h at 37 °C. An aliquot of E.coli cell suspension (4.9 mL) was pipetted out into a sterile petridish in a laminar airflow chamber. To the same petridish, 0.1 mL of the nano catalytic suspension at a concentration of 1 mg/10 mL was added and exposed to the visible light irradiation. After appropriate dilutions in sterile water, aliquots of 1 mL were spread on to agar plates and incubated at 37 °C for 24 hours.

Results and Discussion

X-ray diffraction studies

The XRD patterns of C-1, C-2 and C-3 shown in Fig. 1 reveal that all the catalysts are in the anatase phase as confirmed by (101), (004), (200), (105) and (211) diffraction peaks[18]. From the XRD patterns the characteristic planes of anatase phase with highest intensity peak was observed at 2θ = 25.3° corresponding to 101 plane (JCPDS File No. 21-1272). The average crystallite sizes of the prepared catalyst were calculated from the broadening of the full width at half maximum (FWHM) peaks by using Scherrer's equation (Table 1). The crystallite size of C-1 was found to be in the range of 28.2–35.5 nm, 18.1–20.2 nm for C-2 and 8.2–14.2 nm for C-3 prepared in presence of SDS surfactant medium. From these results, it was concluded that there was large reduction in crystallite size for Co^{2+}-TiO_2 synthesized in presence of SDS surfactant.

UV-visible diffusion reflectance spectroscopy

Figure 2 represents the UV-visible absorption spectra of C-1, C-2, and C-3 nanophotocatalysts. Due

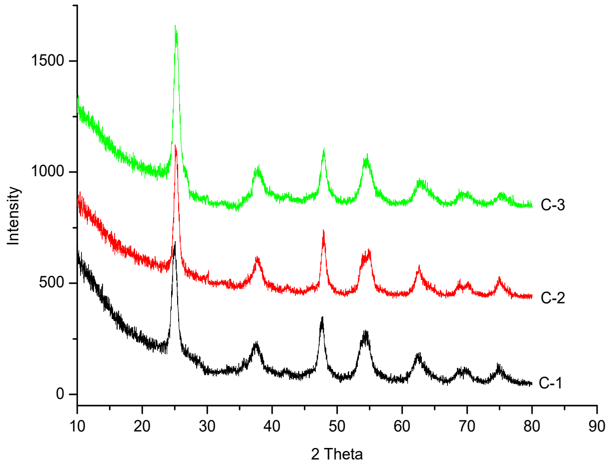

Fig. 1 – XRD patterns of (C-1) undoped TiO_2, (C-2) 0.5 wt.% Co^{2+}-TiO_2, (C-3) 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant).

Table 1 – Crystallite size, band gap and BET data

Catalyst	Crystallite size (nm)	Band gap energy (eV)	BET analysis		
			A_{BET} (m_2/g)	*V*p (cc/g)	Pore width (nm)
Undoped TiO_2 (C-1)	28.2-35.5	3.2	22.6	0.09	6.1
Co^{2+}-TiO_2 (C-2)	18.1 - 20.2	2.52	26	0.082	5.13
Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) (C-3)	8.2 - 13.5	2.48	73.79	0.129	4.54

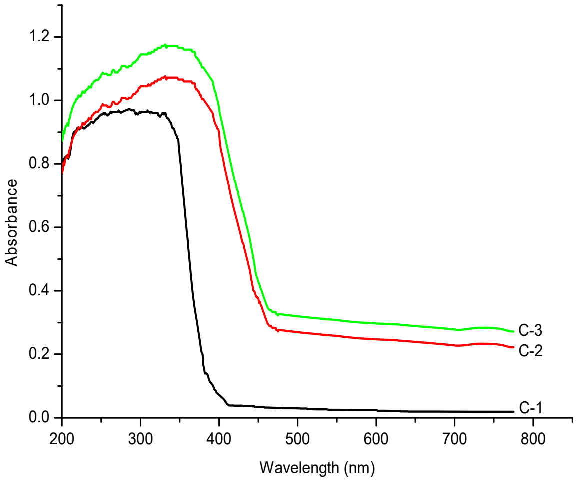

Fig. 2 – UV-visible absorption spectra of (C-1) Undoped TiO_2, (C-2) 0.5 wt.% Co^{2+}-TiO_2 , (C-3) 0.5 wt% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant).

to doping of cobalt into TiO_2 lattice decrease in band gap energy was observed. Due to narrowing of the band gap, absorption was observed more towards visible region (red shift) ranging between 500-700 nm. It was calculated by the equation $E_{bg} = (1240/\lambda)$ and the value are presented in Table 1. For C-2 the band gap is found to be 2.52 eV while it is 2.48 eV for C-3 which was close with that of previous literature values[19]. From this we may conclude that there was a good contact between TiO_2 and Co^{2+} leading to reduction in band gap which enhances the photocatalytic activity in visible light. Lettmann *et al.*[20] reported that there was good relation between light absorption properties and the photocatalytic activity. There was no role of surfactant in reducing the band gap energy but it influenced the decrease in the particle size.

Fourier transform infrared spectroscopy

The FT-IR spectra of (C-1)-undoped titania, (C-2)- 0.5 wt.% Co^{2+}/TiO_2, (C-3)- 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) after calcinations and (C-4)- 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) before calcinations, were recorded (Supplementary Data, Fig. S1). From the spectrum of C-3, peaks located at 3421.17 cm^{-1} and 1633.45 cm^{-1} were attributed to stretching vibrations of O-H and H-O-H bending vibrations of adsorbed water molecules. This confirms the presence of hydroxyl ions in Co^{2+}-TiO_2. For spectrum of C-1, peaks were observed at 3407.61 cm^{-1} and 1633.16 cm^{-1} corresponding to O-H and H-O-H bending vibrations of adsorbed water molecules. Below 1000 cm^{-1} stretching vibrations were observed at 654.03 cm^{-1} for undoped TiO_2 where as for C-3 it was observed at 703.94 cm^{-1} corresponding to the Ti–O–Ti. This small deviation observed may be due to Co doped substitutionally in the TiO_2 matrix. From spectrum of C-4 the peaks located at 3133.84 cm^{-1}, 2395.61 cm^{-1} correspond to the peaks of H-C-H-stretching frequencies. Along with the peaks at 1762.82cm^{-1}, 1628.93 cm^{-1}, prominent peaks were observed at 1384.68 cm^{-1}, and 825.59 cm^{-1} and these correspond to S=O asymmetric, symmetric stretch and S-O-R stretching frequencies. These were comparable with that of the characteristic absorption peaks of SDS surfactant. From this it was confirmed that SDS was present during the synthesis of the catalyst. The slight alteration in the stretching frequencies when compared with that of surfactant were due to the bond formed due to interaction between the surfactant towards the cobalt doped titania during encapsulation. Absence of these peaks from spectrum of C-3 confirmed that there was no surfactant present in the synthesized catalysts after calcinations at 450 °C. This clearly signified the importance of surfactant and its influence in the synthesizing particles with much reduced in size.

BET analysis

From the BET analysis, nitrogen adsorption/desorption isotherms at 77 K and parameters such as surface area (A_{BET}), pore volume (V_p) and average pore size (S_p) were determined. The surface area was determined by the multipoint BET (Brunauer-Emmett-Teller) method using the adsorption data in the relative pressure (p/p_0). The BJH (Barrett-Joyner-Halenda) method was applied to determine the pore volume and the average pore size of all the catalysts. Surface area A_{BET} (m^2/g), pore volume (cc/g) and pore size (nm) of the catalysts are represented in Table 1. From these results, the surface area for C-1 was found to be 22.6 m^2/g, 26 m^2/g for C-2 and 73.79 m^2/g for C-3. The results obtained are higher than the values reported from in the literature[21]. This signifies the influence of the SDS surfactant in synthesizing the particles with reduced size and increase in surface area of the catalyst. Due to increase in surface area dye adsorbs at a greater extent which was evident from the later degradation of the methyl red. Figure 3(a) represented N_2 adsorption-desorption isotherms of C-3. From the isotherm it was observed that at maximum and

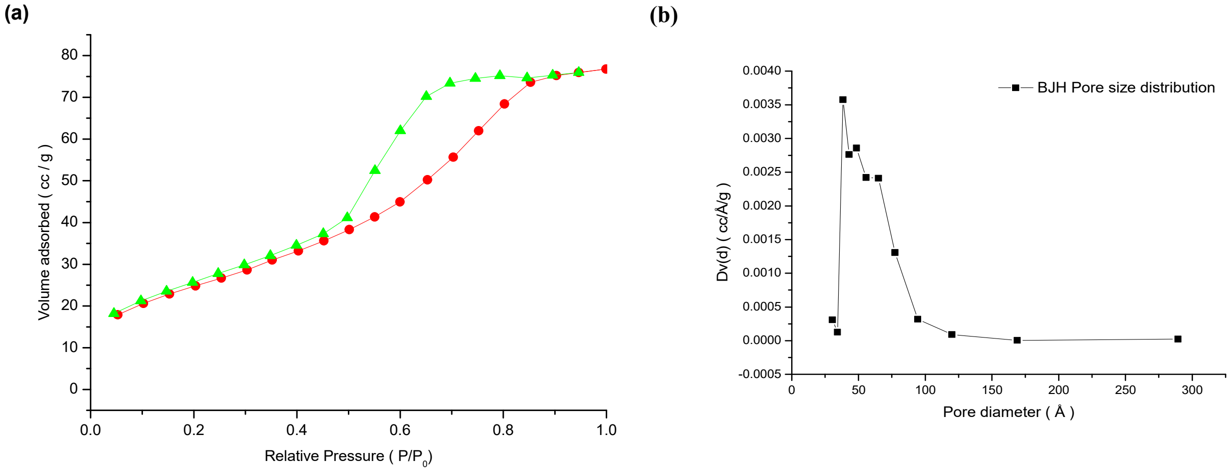

Fig. 3 – (a) Nitrogen adsorption and desorption isotherms of Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant), and, (b) BJH pore size distribution of Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant).

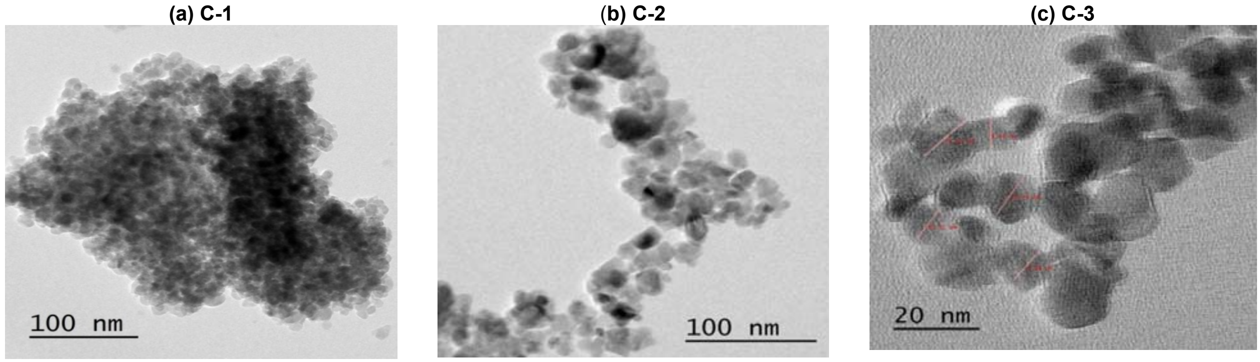
(a) C-1 **(b) C-2** **(c) C-3**

Fig. 4 – HR TEM images of (a) (C-1) undoped TiO_2, (b) (C-2) 0.5 wt.% Co^{2+}-TiO_2, and, (c) (C-3). 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant).

minimum relative pressure as 0.96 and 0.5 the curve exhibited hysteresis loop and was represented as H_2 type. These were described as ink-bottle pores with narrow necks and wider bodies indicating the presence of mesopores. Hence the catalysts were described as mesoporous adsorbents[22-23]. Figure 3(b) represents the pore size distribution curves of the catalyst C-3 obtained by BJH method. The mesopores of the C-1 are reported with pore volume of the mesopores as V_P = 0.082 cc/g while for C-3 Vp = 0.129 cc/g. These results indicate the pore size distribution ranges from 20 to 40 nm (Table 1). These results clearly indicated surfactant role during the synthesis of the catalyst. Basing on the results catalyst prepared in presence of surfactant having more surface area, pore volume and pore size has shown better absorption of dye molecules on the surface of catalyst leading to increase in photocatalytic degradation[24, 25].

Transmission electron microscopy

The TEM images show the particle size of C-1 ranging from 26–30 nm, while for C-2, it was 18–20 nm and for C-3, the range was found to be 8.40–13.20 nm (Fig. 4). TEM images show decrease in the particle size of the synthesized catalyst. This is due to the influence of SDS surfactant medium, where encapsulation on C-3 has occurred to a greater extent, due to the electrostatic interactions between anionic surfactant and positively charged titania surface.

Scanning electron microscopy

The SEM-image of the undoped TiO_2 appears as large blocks of the coarse material with agglomeration (Fig. 5). The SEM images indicate the change in the morphology of the nanoparticles, where the particles were of rough nature with increase in surface area. From SEM images of C-3, the nanoparticles were found to be as tiny clusters with irregular in shape. This was due to presence of surfactant during the

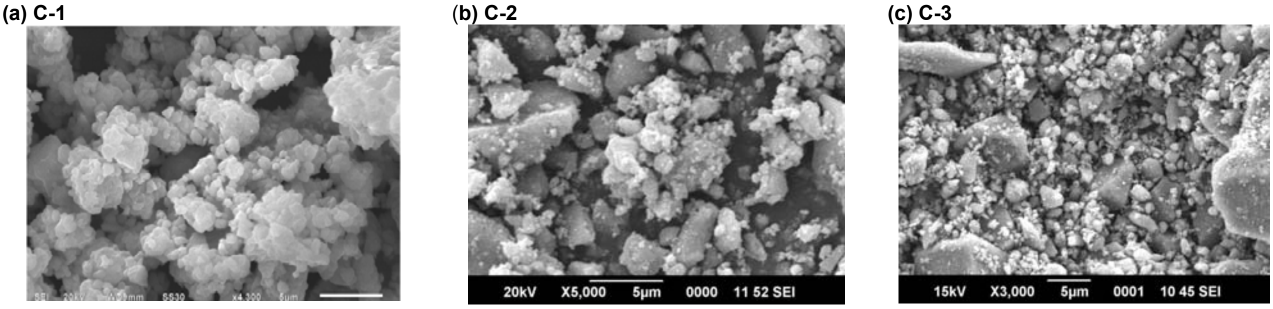

Fig. 5 - SEM images of (a) (C-1) Undoped TiO_2, (b) (C-2) 0.5wt.% Co^{2+}/TiO_2, and, (c) (C-3). 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant).

synthesis of the catalyst which restricted the further growth of particles size.

X-ray photoelectron spectroscopy

From XPS analysis of the catalyst, presence of Co, O, and Ti was confirmed and their oxidation states were established as Co^{2+}, O^{2+} and T^{4+}. High resolution XPS of Ti 2*p*, O 2*p* and Co 2*p* spectra of C-3 respectively are given as Fig. S2 (Supplementary Data). The binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ were found to be at 458.0 eV and 463.7 eV. These values are consistent with the reported binding energies values for Ti^{4+} in TiO_2[26, 27]. The O 1*s* peak was located at 529 eV, While the Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks were located at 779.1 eV and 794.5 eV respectively, which are characteristic of Co^{2+} (ref. 28).

Photocatalytic activity of the Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant)

The photocatalytic efficiency of the catalyst C-3 was estimated by conducting experiments with degradation of methyl red under visible light irradiation. Blank experiments were performed with catalyst in the absence of light where there was no significant change in the methyl red concentration. Similarly the percentage degradation of methyl red was found to be significantly less in the absence of catalysts under visible light. The degradation of methyl red can be enhanced only in the presence of both catalyst and light. It was also observed that the efficiency depends on other parameters such as catalyst dosage, initial concentration of pollutant and pH. To obtain optimum conditions for an efficient photocatalytic degradation of the dye, experiments were conducted by varying each parameter while keeping the other conditions constant.

In order to obtain optimum conditions for dopant concentration a set of experiments were carried out by varying the dopant concentration at 0.25, 0.5, 0.75 and 1.0 wt. % of Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) for the degradation of methyl red by maintaining other conditions constant. The experimental results are shown in Fig. 7. The experimental results have shown that for 0.5 wt. % of the catalyst exhibited superior photocatalytic activity. Hence, it was considered as an optimal dopant concentration. The rate for degradation of methyl red for 0.5 wt. % of the catalyst was found to be 3.45 mg $L^{-1}min^{-1}$. Further for increase in dopant concentration, i.e., for 1.0 wt.% the catalyst, decrease in the photoreactivity was observed. Henc,e further experiments were carried on with 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) (C-3).

The solution pH in a reaction plays an important role in catalysis, which modifies catalyst surface charge. Experiments were carried on to determine the effect of pH by varying pH values ranging from 2-4 by maintaining other parameters constant (Supplementary Data, Fig. S3) Results indicate that the rate of degradation of methyl red was maximum at pH = 3, indicating that acidic environment favors the adsorption of the dye molecules on the catalyst surface. This is due to the electrostatic interactions existing between the two. TiO_2 being positively charged, maximum adsorption was observed with the anionic dye under acidic conditions. At high pH values, the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with dyes[29]. The rate of degradation for 0.5 wt.% Co^{2+}-TiO_2 was found to be maximum at pH = 3 and found to be 5.373 mg $L^{-1}min^{-1}$.

Experiments were performed by varying the concentrations of catalyst from 0.05 to 0.25 g in 100 mL aqueous solution of methyl red while keeping other conditions constant (Supplementary data, Fig. S4). From these results it is clear that the rate of degradation increases linearly with increase in the amount of catalyst up to 0.1 g, and then decreases (leveling off). This is due to increase in the hydroxyl radicals which increased the photocatalytic degradation. However, beyond 0.1 g catalyst dosage, though more surface area was available for dye molecules, solution turbidity increases and this restricts light transmission leading to decreased photocatalytic activity. Hence, 0.1 g of the catalyst was found to be optimal amount of photocatalyst. The observed rate constant at catalyst dosage 0.1g is 6.909 mg L^{-1} min^{-1}.

In order to find out the optimum initial dye concentration, experiments were carried out by varying the dye concentration at 1, 5, 10 and 15 mg L^{-1} by keeping other conditions constant (Supplementary Data, Fig. S5). Optimum initial dye concentration for maximum degradation of methyl red was observed at 5 mg L^{-1}. With further increase in the dye concentration, there was decrease in degradation rate observed may be due to less generation of $OH^{\cdot}$ radicals on the catalyst surface which cover the surface of the catalyst from light intensity. The rate of degradation (7.676 mg $L^{-1}min^{-1}$) of methyl red with the catalyst was found to be maximum at 5 mg L^{-1}.

Based on the experimental results of photocatalytic degradation of methyl red dye it was concluded that 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) was an efficient photocatalyst.

Antibacterial activity studies of Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant)

The antibacterial activity studies on *E. coli* gram negative bacteria by the catalyst C-3 was studied. Serial dilutions were followed to attain bacterial cell concentration colony forming units CFU/mL. Antibacterial efficiency (in percent) was reported using the equation, $(Co–C)\times100/Co$, where *Co* and *C* are the number of colonies formed before and after irradiation. In this study 1 mg/mL of Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) was added to the bacterial cell suspension solution and exposed to visible light irradiation. The number of colonies formed in each experiment was calculated. It was observed that there was decrease in the number of colonies in agar medium plates with increase in time (Supplementary Data, Fig. S6). The antibacterial activity of the C-3 catalyst started in 15 min and increased with increase in exposure time till 60 min Table 2 gives the % survival of *E. coli* after treatment with C-3 photocatalyst. Figure 7 shows the plot between the antibacterial efficiency of the catalyst against irradiation time at different time intervals

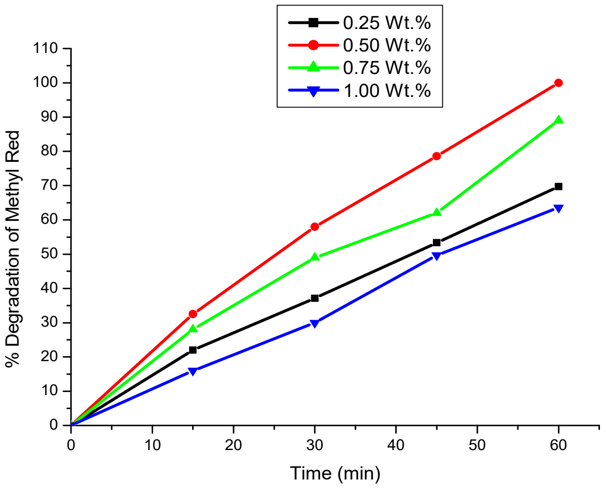

Fig. 6- Effect of dopant concentration on the degradation of methyl red at pH = 3 and dye concentration 10 mg L^{-1}.

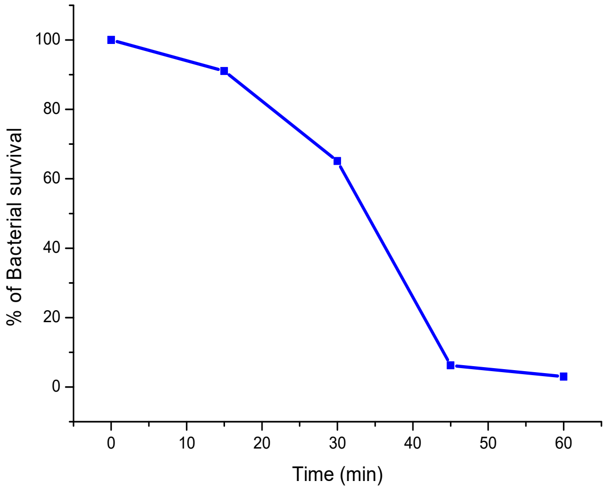

Fig. 7 - Graph showing survival (%) of *E. coli* after treatment with 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant).

Table 2 – Survival (%) of *E. coli* after treatment with 0.5 wt.% Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant)

Time (min)	CFU	% of bacterial survival
Control	1254	Nil
0	562	100
15	168	91.07
30	86	65.11
45	48	6.25
60	6	3

from 15 min to 60 min. It is observed that with increase in exposure time there was increase in the antibacterial activity. Within 60 min exposure, almost complete elimination of bacterial colonies was observed. Bacterial cell wall was firm and played a vital role in the maintenance of cell morphology. The outer membrane of *E. coli* was made of lipopolysaccharide (LPS, a phospholipid layer) and peptidoglycan (periplasm) which gives strength to the cell wall providing mechanically, a strong network without this support the cell would break apart[30,31].

5.2. Photocatalytic mechanism for bacterial inactivation by the catalyst

Cobalt doped catalyst when illuminated with visible light irradiation it results in formation of the pairs of free electrons and holes in the conduction and valence band region of titania. These react with oxygen and adsorbed hydroxyl group to produce further reactive oxygen species (ROS) such as superoxide ($O^{\bullet}{}_2^-$), hydroxyl radicals ($OH^{\bullet}$), H_2O_2 etc. These can cause fatal damage to microorganisms. These species could decompose outer membranes. The damage of peptidoglycan changes the morphology of E. coli Without the protection of peptidoglycan and phospholipid layer, the leakage of the interior substances would occur and the cells subsequently die[32-34]. Thus from these results it was clear that Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) was successful in killing of *E. coli* under visible light irradiation and can be used as efficient antibacterial agent.

Mechanism for photocatalytic degradation of dye and bacterial inactivation

The following mechanism is proposed for the photocatalytic reactions Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) based on the above experimental results. Due to doping of cobalt into TiO_2 lattice, electrons are trapped by cobalt ions and are further scavenged by molecular oxygen, which is adsorbed on the TiO_2 surface to generate superoxide radical, hydrogen peroxide (H_2O_2), hydroperoxy ($HO_2^{\bullet}$) and hydroxyl (•OH) radicals[35]. Formation of (•OH) radicals played an important role in the photocatalytic degradation of methyl red pollutants.

$$Co^{2+}\text{-}TiO_2 + h\nu \longrightarrow Co^{2+}\text{-}TiO_2\ h^+_{vb} + Co^{2+}\text{-}TiO_2\ e^-_{cb}$$

$$Co^{2+} + e^- \longrightarrow Co^+ \text{(unstable)}$$

$$Co^+ + O_2 \longrightarrow Co^{2+} + O_2^{\bullet -}$$

$$H_2O \longrightarrow OH^- + H^+$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$$

$$2HO_2^{\bullet -} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 + e^-_{trapped} \longrightarrow {}^{\bullet}OH + OH^-$$

$$OH^- + h^+_{vb} \longrightarrow {}^{\bullet}OH$$

Degradation of methyl red in the solution takes place due to the positive holes in the valence band which act as good oxidizing agents.

$$OH \text{ (or } h^+_{vb}) + MR\ (C_{15}H_{15}N_3O_2) \longrightarrow MR^+$$

$$MR^+ \longrightarrow \text{Degradation products}$$

Here 'Red' is the methyl red an electron donor (reductant). Methyl red was attacked by the hydroxyl radicals formed both by trapped electrons and hole in the VB as given in the above equations, to generate organic radicals or other intermediates which further undergo degradation and thus degradation of methyl red takes place finally changing into colorless solution with generation of organic radicals and other intermediates.

Considering the mechanism for bacterial inactivation, the reactive oxygen species (ROS) of catalyst play key role in the production of hydroxyl radicals (•OH).These strong oxidants react with peptidoglycan of bacteria and finally results in destruction of bacteria.

$$\text{Bacteria} + {}^{\bullet}OH \longrightarrow \text{Bacterial destruction}$$

Thus the catalyst is found to be efficient in degradation of methyl red and in killing of bacteria.

Conclusions

Assisted by sodium dodecyl sulfate through sol-gel method, Co^{2+}-TiO_2 (0.5wt.%) (catalyst prepared in presence of SDS surfactant) nanophotocatalyst was successfully prepared. The catalyst was synthesized with decreased particle size and increased specific surface area and this was due to the influence of the surfactant during its synthesis. All the samples were found to be in the anatase phase. From UV-DRS spectra of the catalyst, there was shift towards visible region (red shift) with decrease in band gap. This was due to doping of cobalt into TiO_2. Existence of cobalt as Co^{2+} was confirmed from XPS analysis. From BET analysis, catalyst particles were reported with increase in specific surface area. The SEM images indicated the change in the morphology with tiny irregular particles. Particles size of the catalyst was decreased and found to be in the range 8.4–13.2 nm. FT-IR studies indicated cobalt as a substitutional dopant into TiO_2. The efficiency of the photocatalyst was investigated by degradation of methyl red. The optimum conditions for the degradation of methyl red dye with catalyst include 0.5 wt.% of dopant concentration, 0.1 g catalyst dosage, pH 3 with 5 mg L^{-1} initial dye concentration, under which the rate of degradation of methyl red solution was found to be 7.676 mg $L^{-1}min^{-1}$. The catalyst was found effective towards the destruction of bacteria, *E. coli*, which was observed by the decrease in bacterial colony growth within 60 min. Thus, the 0.5 wt. % Co^{2+}-TiO_2 (catalyst prepared in presence of SDS surfactant) has been proved to be an excellent nanophotocatalyst towards photocatalytic degradation of methyl red as well as an antibacterial agent.

Supplementary Data

Supplementary Data associated with this article, viz., Figs S1-S6, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(3)278-286_SupplData.pdf.

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