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## Synergistic Effects of Phosphorus and Cobalt Binary Doping on Visible Light Activity of TiO<sub>2</sub> by Sol-Gel Method and Evaluation of Photocatalytic Efficiency

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### ABSTRACT

Phosphorus and cobalt codoped TiO<sub>2</sub> nanomaterial was successfully prepared by single step sol-gel method by doping different weight percentages of dopants concentrations into TiO<sub>2</sub> lattice. The codoped TiO<sub>2</sub> samples were characterized to confirm the structural and morphological changes in TiO<sub>2</sub> crystal lattice by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), transmission electron microscopy (TEM), UV-visible diffuse reflectance spectroscopy (UV-vis. DRS), X-ray photo electron spectroscopy (XPS), Brunauer-Emmett-Teller surface area analyzer (BET) and Fourier transform infrared spectroscopy (FT-IR). The characterization results revealed that all the codoped samples show anatase phase, nanoparticle (5.8 nm) and narrow band gap (2.54 eV). These results enhance the photocatalytic activity of codoped TiO<sub>2</sub> in visible light for the degradation of Fast Green dye within 60 min.

### 1. Introduction

Every procedure has its own limitations for waste water treatment, but among the semiconductors nano sized TiO<sub>2</sub> in anatase form was the more promising semiconducting material for environmental applications due to its high photo-reactivity [1, 2], chemical stability, good durability in hostile environments, Bio-compatibility, water insolubility and non-photo corrosive nature, but photoactive in Ultraviolet region. To obtain the visible light active TiO<sub>2</sub> many attempts has been made to get visible light activity by many researches has been carried out by doping with metals [3-7], non-metal [8-15], and codoping [16] with metal-metal and metal-nonmetal. Among these codoping combinations metal-nonmetal codoping shows improved the photocatalytic activity of TiO<sub>2</sub> in visible light due to enhancing the electron-hole pairs separation, reduced electron recombination processes, decrease in grain size and active under visible light irradiation. According to literature survey, among non-metals, phosphorus (P) doping [17] is found to be most photocatalytic activity of TiO<sub>2</sub> due to increase in the surface area and stabilizing anatase [18-20] structure. Whereas in metals cobalt (Co) doping decreases the electron-hole pair recombination rate and acts as electron trap [21, 22] enhances the photocatalytic activity [23]. Hence, in the present investigation phosphorus (P) and cobalt (Co) have been selected for the synthesis of P,Co-codoped TiO<sub>2</sub> nanomaterial by using sol-gel method. Among all the methods available, sol-gel method is advantageous because homogeneity, high purity, low temperature and stoichiometric control than precipitation [24], hydrothermal [25] chemical vapour deposition [26], electrospinning [27] and so on. The photocatalytic activity of as prepared catalyst was verified by the degradation of Fast Green dye. Fast Green dye is a non-biodegradable and mutagenic in nature. Thus Fast Green dye has been widely used in textile industry. To minimize the Fast Green pollution in the environment many researchers have been under taken various methods [28] to degrade the Fast Green dye by using adsorption over de-oiled soya and bottom ash, aqueous suspension of titanium dioxide, *Azadirachta indica* (neem) Leaf powder [29], electro generated Fenton reagent at carbon felt cathode [30], and ZnO [31] as photocatalyst. But there was no attention paid towards photocatalytic degradation of Fast Green dye using nanosized P,Co-Codoped TiO<sub>2</sub> so far.

### 2. Experimental Methods

#### 2.1 Materials Required

Titanium tetra-n-butoxide (E-Merck, Germany), Triethyl phosphate (E-Merck, Germany), Cobalt(II)nitrate (Sigma Aldrich, USA) were used as precursors for Ti, P and Co respectively. All the chemicals used in the synthesis process were reagent grade and the solutions are prepared in double distilled water without further purification.

#### 2.2 Synthesis of Phosphorus, Cobalt Co-Doped TiO<sub>2</sub> Nanomaterial

Phosphorus and Cobalt codoped TiO<sub>2</sub> samples were prepared by varying the dopant concentrations with respect to amount of TiO<sub>2</sub>. 15 mL of titanium tetra-n-butoxide along with 30 mL of absolute ethanol taken in a 150 mL pyrex glass beaker and stirred for 10 min. 2.1 mL of HNO<sub>3</sub> was added drop wise to this solution and continue the stirring upto 30 min. This solution was further considered as solution I. In another beaker 30 mL of absolute ethanol and 4.32 mL of H<sub>2</sub>O along with the dopants i.e triethyl phosphate and cobalt nitrate were taken as per the required amounts of dopants with respect to TiO<sub>2</sub> (solution II) and stirred the solution for 30 min. Solution II was added to solution I from the burette slowly under continuous vigorous stirring at room temperature until the transparent sol was formed and again continue the stirring for 2 h at room temperature. The sol obtained was kept in dark for 48 h to ageing for gel formation. The gel was dried in an oven at 100 °C and ground. The catalyst powder was calcined at 450 °C in a muffle furnace for 5 h, cool the catalyst powder to room temperature and ground. The same procedure was adopted for the preparation of undoped TiO<sub>2</sub> without addition of dopants. All the catalysts samples and undoped samples prepared were given code numbers and tabulated in the Table 1.

**Table 1** Name assigned to different weight percentage of TiO<sub>2</sub> co-doped catalysts

S.N	Code name of the samples	Wt% of dopants doped into TiO <sub>2</sub>	
		Phosphorus	Cobalt
01	PCT <sub>1</sub>	0.75 w%	0.25 w%
02	PCT <sub>2</sub>	1.0 w%	0.25 w%
03	PCT <sub>3</sub>	0.50 w%	0.50 w%
04	PCT <sub>4</sub>	0.25 w%	0.75 w%
05	PCT <sub>5</sub>	0.25 w%	0.25 w%
06	Pure TiO <sub>2</sub>		

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### 2.3 Instrumental Techniques

The synthesized photocatalysts were characterized by various sophisticated analytical techniques. UV-vis & DRS spectra are taken by using Shimadzu 3600 UV-vis & DRS NIR spectrophotometer with an integrating sphere diffuse reflectance is used. XRD patterns of the samples were recorded by using Ultima IV, RIGAKU Model with Anode Cu-WL1  $\lambda=1.5406$  nm, nickel filter-current-40 mA, Voltage-40 kV, with  $2\theta$  scanning range 5.000-90.9505, scan rate of  $10.1600$  s<sup>-1</sup>. XPS was recorded with a PHI quantum ESCA microprobe system, using the AlK $\alpha$  line of a 250W X-ray tube as a radiation source with the energy of 1253.6 eV, 16 mA  $\times$  12.5 kV and working under the pressure lower than  $1 \times 10^{-8}$  Nm<sup>-2</sup>. Morphology and size of the anatase particles was determined by SEM Model JSM-6610 LV equipped with an energy dispersive X-ray (EDS) voltage 20 kV. BET is a used to determine pore size, pore volume and surface area of anatase particles from N<sub>2</sub> adsorption desorption isotherm at 77.3 K, Model-NOVA 2200 E system. TEM was determined by TECNAI FE12 TEM operated at voltage-120 kV. FT-IR spectra were recorded by using FT-IR spectrometer Model-Nicolot Avatar-360. Fast Green degradation was monitored by using UV-vis spectrophotometer model - Shimadzu 1601.

### 2.4 Photocatalytic Activity Measurements

The high pressure mercury metal halide lamp (400 W) with UV filter Oriol no: 51472 was placed 20 cm away from the reaction mixture. To remove IR radiation source and to keep the reaction mixture at room temperature the running cool water was circulated around the sample container. The photocatalytic procedure was carried out with a required amount of catalyst dosage added to fresh 100 mL of aqueous dye solution containing 10 mg/L dye taken in a Pyrex glass vessel with continuous stirring. Prior to irradiation the solution was adjusted to required pH by the addition of either 0.1 N HCl or 0.1 N NaOH. The solution was continued the stirring for 30 min in dark to achieve the adsorption and desorption equilibrium between dye and catalyst surface and then exposed to visible light. Then 5 mL aliquots of samples were withdrawn from the reaction mixture by using millipore syringe (0.45  $\mu$ m) at different time interval and measure the absorption of the sample at  $\lambda_{\text{max}}$  620 nm by using UV-VIS spectrophotometer (Milton Roy Spectronic 1201). The percentage of degradation of the dye (Fast Green) was calculated by using the following equation.

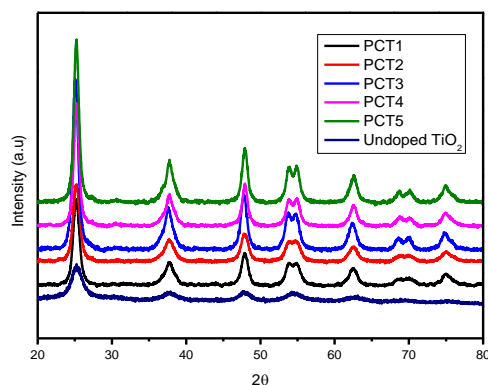
$$\% \text{ of Degradation} = A_0 - A_t / A_0 \times 100$$

where,  $A_0$  is initial absorbance of dye solution before exposure to light and  $A_t$  is absorbance of dye solution at time t after exposure to light.

## 3. Results and Discussion

### 3.1 X-Ray Diffraction Studies (XRD)

The powder X-ray diffraction patterns of undoped and co-doped (phosphorus and cobalt) TiO<sub>2</sub> were recorded (Fig. 1) at  $2\theta = 20^\circ$  to  $80^\circ$ . For all the undoped and codoped samples the maximum peak were observed at  $2\theta = 25.14^\circ$  indicated that the formation of anatase phase [JCPDS NO:21-1272] [32]. The other peaks were observed at  $2\theta$  of  $37.83^\circ$ ,  $47.88^\circ$ ,  $54.87^\circ$ ,  $74.83^\circ$  and  $82.56^\circ$  with indices corresponding to (004), (200), (211), (215), (224) planes respectively and also coincide with that of undoped TiO<sub>2</sub> indicates that codoping did not influence the anatase phase of TiO<sub>2</sub>.



**Fig. 1** XRD pattern of the synthesized undoped and codoped TiO<sub>2</sub> with different wt% of P<sup>5+</sup> and Co<sup>2+</sup>

There are no characteristic peaks were observed for phosphorus and cobalt oxides in XRD spectrum in all the codoped samples which indicates

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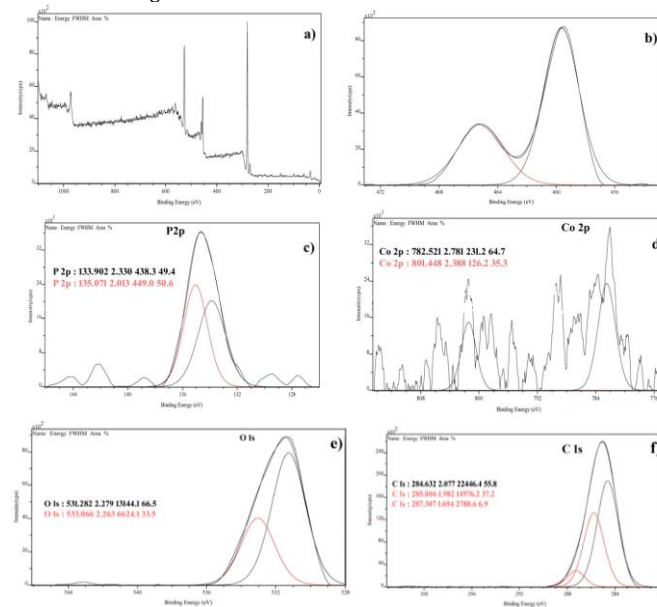
that the phosphorus and cobalt ions are incorporated into the lattice of anatase TiO<sub>2</sub> in place of Ti<sup>4+</sup> ion. According to the FWHM analysis of the anatase diffraction peak and based on the Scherrer's formula [33], the average crystallite size of undoped and codoped TiO<sub>2</sub> samples were found to be 36.8 nm and 5.7 nm - 12.1 nm. From these results decrease in crystallite size was observed due to codoping of cobalt and phosphorus into TiO<sub>2</sub> lattice. The variation in the particle size and the phase content demonstrated that P doping decreases the particle size, aggravate the unit cell distortion, retards the phase transformation of anatase to rutile [34] and the reducing atmosphere due to P-doping was more efficient in slowing down the crystal-growth rate in P, Co-codoped TiO<sub>2</sub> [35, 36]. The comparative results of pure TiO<sub>2</sub>, single doped, phosphorus and cobalt codoped crystallite size with codoped TiO<sub>2</sub> are given in the Table 2. The results from Table 2 confirm that the P,Co co-doped samples having less crystallite size compared to that of phosphorus and cobalt single doped TiO<sub>2</sub> samples in which PCT1 show less crystallite size (8.1 nm).

**Table 2** A comparison of band gap and crystallite size of undoped, single doped and co-doped TiO<sub>2</sub>

S.No.	Catalyst code	Band gap, eV	Crystallite size, nm
01	Undoped TiO <sub>2</sub> (T)	3.58	15.31
02	P-doped TiO <sub>2</sub> (PT)	3.15	6.8
03	Co-doped TiO <sub>2</sub> (CT)	3.65	19.90
04	P,Co-codopedTiO <sub>2</sub> (PCT)	2.54	5.8

### 3.2 X-Ray Photo Electron Spectroscopy (XPS)

X-ray photo electron Spectroscopic analysis study were carried out to confirm the presence of Ti, P, Co, O and C, and analysed their chemical state. Fig. 2(a) shows the survey spectra of 0.75 wt% of P and 0.25 wt% of Co co-doped TiO<sub>2</sub> and their magnifying spectra of Ti, P, Co, O and C were shown in the Figs.2b-2f.



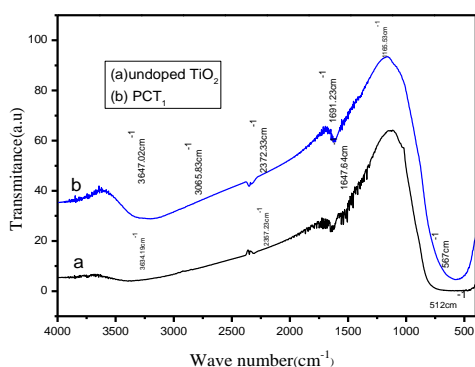
**Fig. 2** a) XPS survey spectrum of co-doped TiO<sub>2</sub> and high resolution spectrum of (b) Ti 2p (c) P 2p (d) Co 1s (e) O1s and (f) C1s

The binding energies of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> (Fig. 2b) components of PCT<sub>1</sub> catalyst are located at 459.653 eV and 465.218 eV [37] which corresponds to Ti<sup>4+</sup> ion in TiO<sub>2</sub> lattice. The doublet peak (Fig. 2c) of P 2p<sub>3/2</sub> and P 2p<sub>1/2</sub> corresponding binding energies at 134.116 eV and 135.222 eV respectively. This indicated that the presence of P<sup>5+</sup> ion in TiO<sub>2</sub> lattice as a substitutional dopant by replacing Ti<sup>4+</sup> ion [17]. This results attributed that P ion present as P<sup>5+</sup> ion but not as PO<sub>4</sub><sup>3-</sup> ion. As per the literature reports if P presents as phosphate ion the binding energy should appear at 133.7 eV [38]. In the present case the binding energies appears at higher side. Hence the P cannot present as a phosphate ion. This result coincides with XRD results. This suggesting that P ions in pentavalent oxidation state ascribing the existence of Ti-O-P bonds. It is important to note that no Ti-P bond is present since no peak was observed at 129 eV where P atom replaces O atom in TiO<sub>2</sub> crystalline lattice [39]. The replacement of Ti<sup>4+</sup> by P<sup>5+</sup> caused a charge imbalance has been compensate this effect, by reducing the number of oxygen vacancies resulting in the enhancement of the photo catalytic activity [40]. The doublet peak (Fig. 2d) of cobalt 2p<sub>3/2</sub> and cobalt 2p<sub>1/2</sub> peaks are located at binding energies of 782.52 eV and 801.448 eV respectively, which indicated that, a shift towards positive value due to phosphorus doping. These peaks confirms the presence of

cobalt in TiO<sub>2</sub> lattice as Co<sup>2+</sup> oxidation state as a substitutional dopant occupying the Ti<sup>4+</sup> site in TiO<sub>2</sub> lattice [41, 42]. From the Fig. 2(e) 1s spectrum of O shows two peaks at 530.646 eV and 532.554 eV and a strong peak at 530.646 eV is attributed to lattice oxygen in Ti-O bond and a small peak at 532.554 eV corresponding to adsorbed oxygen species such as O and OH groups on the surface of TiO<sub>2</sub> codoped catalyst [43].

### 3.3 Fourier Transform-Infra Red Spectroscopy (FT-IR)

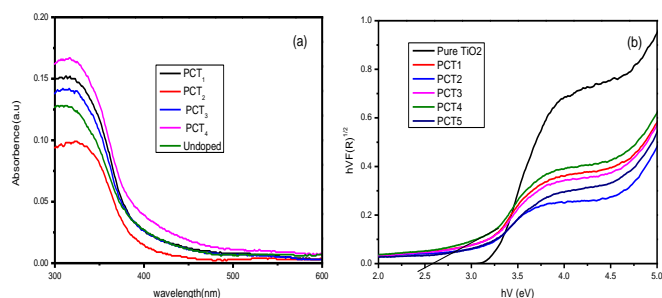
The FT-IR spectra of undoped and P,Co-codoped TiO<sub>2</sub>(PCT<sub>1</sub>) nanomaterials illustrated in Fig. 3 that the peaks at 3474 cm<sup>-1</sup> and 1647cm<sup>-1</sup> corresponding to stretching and bending vibrations of O-H [44] and H-O-H [45] of both the catalysts (undoped and co-doped) respectively. The stretching frequency band at 512 cm<sup>-1</sup> corresponding to Ti-O-Ti network which coincides with literature value [46, 47]. This band shifted to 567 cm<sup>-1</sup> in the codoped samples. Due to codoping, the Ti-O-Ti network was destroyed, a new peaks are arises at 549 cm<sup>-1</sup> and 679 cm<sup>-1</sup> which are attributed to the formation of Ti-O-P or Ti-O-Co or Co-O-P [48]. This can also be explained in terms of new interactions of dopants causes deformation in octahedral symmetry of Ti<sup>4+</sup> in TiO<sub>2</sub> lattice [49].



**Fig. 3** FT-IR spectra of (a) undoped TiO<sub>2</sub> and (b) 0.75 wt% of P<sup>5+</sup> and 0.25 wt% of Co<sup>2+</sup> co-doped TiO<sub>2</sub> (PCT<sub>1</sub>)

### 3.4 Ultra Violet - Visible Diffuse Reflectance Spectroscopic Studies (UV-Vis. DRS)

UV-Vis. DRS spectra of undoped and co-doped TiO<sub>2</sub> samples were given in Fig. 4(a). It is observed that the co-doped samples have a profound effect on its optical response in the visible wavelength range. Compared to undoped TiO<sub>2</sub> the extension of absorption edge towards longer wavelength (red shift) for co-doped samples indicated the decrease in band gap. This is may be due to the formation of an extra energy level above the valance band by P<sub>2p</sub> and O<sub>2p</sub> states in codoped TiO<sub>2</sub> samples. Further it was supported by the calculated band gap energies of the all synthesized samples from the reflectance spectra using the Kubelka-Munk formalism and Tauc plot method [50] as shown in Fig. 4(b). The undoped TiO<sub>2</sub> exhibited the band gap of 3.12 eV which is comparable with the literature value [51] and the co-doped TiO<sub>2</sub> samples showing the band gap ranging from 2.54 to 2.67 eV. Among all the co-doped samples PCT<sub>1</sub> exhibiting less band gap energy i.e 2.54 eV. Cobalt doping forms extra energy level between within the band gap and acts as electron-trap center and enhances electron-holes pair's separation leads to increase in photocatalytic activity of codoped samples PCT<sub>1</sub>. Thus the results indicated that all the co-doped samples are visible light active leads to better photocatalytic degradation efficiency by formation of photo generated electron/hole pairs.



**Fig. 4** (a) UV-vis absorption spectra of as prepared samples and (b) Tauc Plot

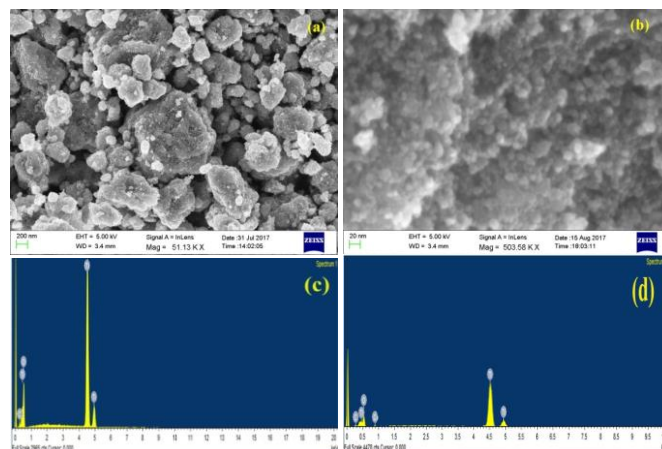
The DRS spectra of undoped TiO<sub>2</sub> and co-doped TiO<sub>2</sub> with different wt% of P<sup>5+</sup> & Co<sup>2+</sup> (b) Tauc plots of the square root of the Kubelka-Munk function (F(R)hv)<sup>1/2</sup> vs photon energy (hv) for determining bandgap energy values.

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### 3.5 Scanning Electron Microscopy - Energy Dispersive X-Ray Studies

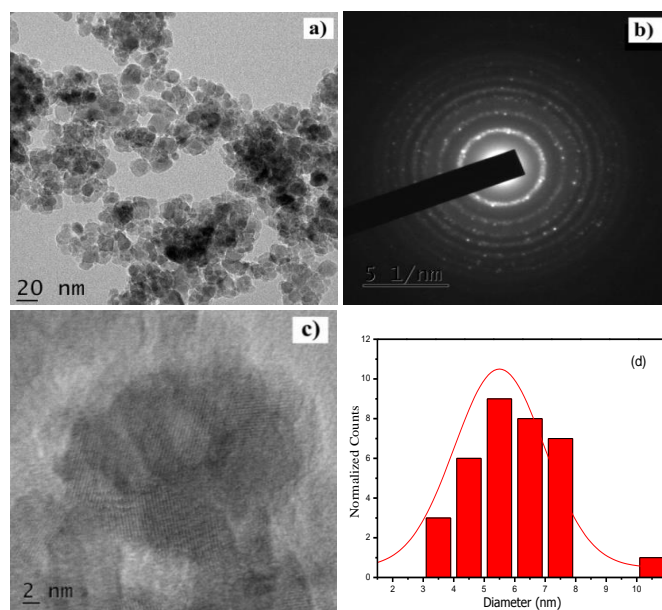
Figs. 5(a) and (b) show typical scanning electron microscopic images of undoped and 0.75 wt% of P<sup>5+</sup> and 0.25 wt% of Co<sup>2+</sup> co-doped TiO<sub>2</sub> (PCT<sub>1</sub>) indicated these particles are in spherical shape, smooth surface and little agglomeration. From the SEM results it can be concluded that agglomeration and particle sizes are decreased [36] greatly in PCT<sub>1</sub> due to codoping of P and Co into TiO<sub>2</sub> lattice and their presence was confirmed by EDX analysis Fig. 5(d).



**Fig. 5** The SEM images of (a) undoped TiO<sub>2</sub> (b) PCT<sub>1</sub>, and the EDS spectrum of (c) undoped TiO<sub>2</sub> and (d) PCT<sub>1</sub>

### 3.6 Transmission Electron Microscopy (TEM)

TEM images of undoped and co-doped TiO<sub>2</sub> samples are given in Figs. 6(a) and (b). In these images it is observed that codoped TiO<sub>2</sub> samples show less particle size than that of undoped TiO<sub>2</sub>. Fig. 6(c) depicted the selected area electron diffraction (SAED) pattern of the PCT<sub>1</sub>, clearly indicated the defined concentric rings which were obtained due to the diffraction from the (101), (004), (200), (211) planes of the anatase TiO<sub>2</sub>. The average particle size of undoped and codoped samples were calculated by the Gaussian fitting of the size histogram as shown in the Fig. 6(e) and found to be 4.8 nm. These results strongly confirmed that, the co-doping of P and Co in TiO<sub>2</sub> lattice decreased the particle size. These results strongly confirmed that, the co-doping of P and Co in TiO<sub>2</sub> lattice decreased the particle size.

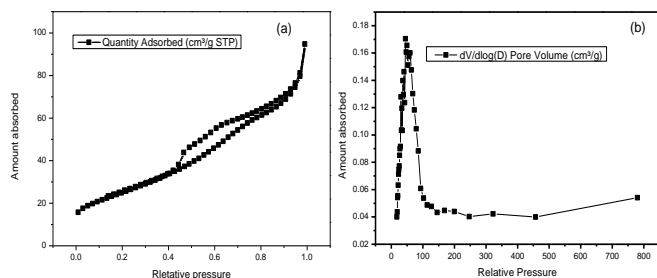


**Fig. 6** TEM images of (a) 0.75 wt% of P<sup>5+</sup> & 0.25 wt% of Co<sup>2+</sup> co-doped TiO<sub>2</sub>, (b) SAED pattern (c) HRTEM image and (e) Histogram showing particle distribution of 0.75 wt% of P<sup>5+</sup> & 0.25 wt% of Co<sup>2+</sup> co-doped TiO<sub>2</sub>

### 3.7 BET - Surface Area Analysis

Accordingly, the BET specific surface area for prepared five samples show an increase than the undoped TiO<sub>2</sub> indicates microspore which in turn provides highest photocatalytic activity for PCT<sub>1</sub> towards Fast Green dye. Nitrogen adsorption-desorption isotherms and their corresponding

Berret- Johner- Halenda (BJH) pore size distribution plot of PCT1 catalyst are presented Fig. 7 and it is inferred that PCT1 is a mesoporous material showing type IV isotherm. Among all the co-doped samples PCT<sub>1</sub> shows high surface area with 9.8549 m<sup>2</sup>/g, pore volumes 0.11567 cm<sup>3</sup>/g and pore size 50.92 Å. These values are higher than non-porous TiO<sub>2</sub> material. Our findings clearly indicates that P,Co co-doped TiO<sub>2</sub> have a larger surface area and greater N<sub>2</sub> adsorption capacity than pure TiO<sub>2</sub>, which is due to the increase in the pore size.



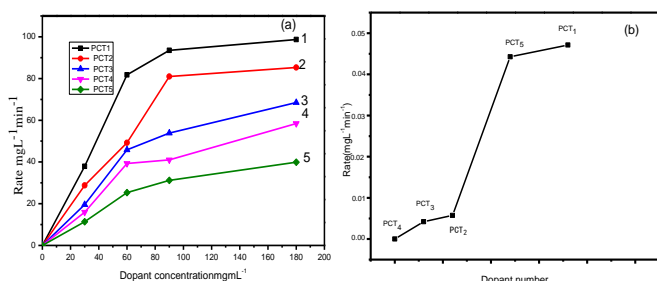
**Fig. 7** BET isotherm data revealing the mesoporus nature of the P,Co codoped TiO<sub>2</sub> sample PCT<sub>1</sub>

### 3.8 Degradation of Fast Green (FG)

In order to measure the photocatalytic efficiency of synthesized nano catalyst PCT<sub>1</sub> the experiments were carried out by varying the reaction parameters such as effect of dopant concentration, initial pH, catalyst dosage and initial dye concentration. Initially blank experiments were performed with dye in presence and absence of visible light and another reaction along with synthesized nano catalyst in presence and absence of visible light and another reaction along with synthesized nano catalyst in presence and absence of light were performed. In both the reactions there is no significant degradation was observed. But in the second reaction a complete degradation was observed without visible light in both the cases. But in the second case reaction a complete degradation was observed in visible light. This clearly demonstrated that for Photocatalytic degradation of FG dye both catalyst and visible light are necessary. To obtain the complete degradation of the dye there is a need to evaluate optimum conditions by studying the effects of reaction parameters.

#### 3.8.1 Effect of Dopant Concentration

To determine the rate of photocatalytic degradation of Fast Green (FG) dye solution a series of experiments were conducted by using the synthesized catalysts with different dopant concentrations were presented in Figs. 8 (a) and (b). All the co-doped samples have higher photocatalytic activity than undoped TiO<sub>2</sub> under visible light irradiation. This indicated that co-doping has improved the photo catalytic performance of TiO<sub>2</sub> in visible light. Among all the co-doped catalysts, PCT<sub>1</sub> shows highest rate to at these dopants concentrations (0.75 wt% of P<sup>5+</sup> & 0.25 wt% of Co<sup>2+</sup>) there is an increase in number of trapped charge carriers per particle [52]. Further increase in dopant concentration the rate decreases, this is may be attributed that the average distance between trap sites decreases with increasing the number of dopants confined within a particle [53].



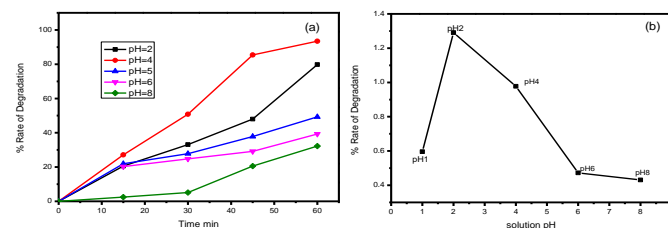
**Fig. 8** The Effect of dopant concentration on photocatalytic activity of co-doped titania by degradation of Fast Green. Here, catalyst dosage 10 mg and [FG] 10 mg/L

#### 3.8.2 Effect of pH

pH is proposed to be a major factor influencing the rate of photocatalytic performance [54] of the catalyst. To understand the effect of pH, experiments were carried out by varying the pH from 1 to 8 by kept the other parameters constant and the experimental results are presented in the Figs. 8(a) and (b). The results indicated that the rate of degradation increases with increase of pH up to 2, later this rate decreases. When the pH is less than 2, the degradation of Fast Green slowly increases, it may be

due to the increase in the production of OH<sup>•</sup> radicals and their existence leads to competition between dye negative(-ve) molecules and OH<sup>•</sup> radicals. Further the rate will be increased as OH<sup>•</sup> radicals consumption increase for the degradation of adsorbed dye molecules. In acidic pH the percentage of degradation of FG was found to be high at pH 2, at which the positive charge (H<sup>+</sup> ions) on TiO<sub>2</sub> surface increases and negatively charged dye molecules can easily adsorbed its surface, which leads to high percentage of degradation of dye. When the pH increased to basic medium the catalyst surface changes to negative and electrostatic repulsion with the same charge on the dye molecules, which causes a decrease in the rate of degradation as shown in the Figs. 9(a) and (b). The rate of degradation of FG increases up to pH 2 further rate slowly decreases as H<sup>+</sup> ions decreases.

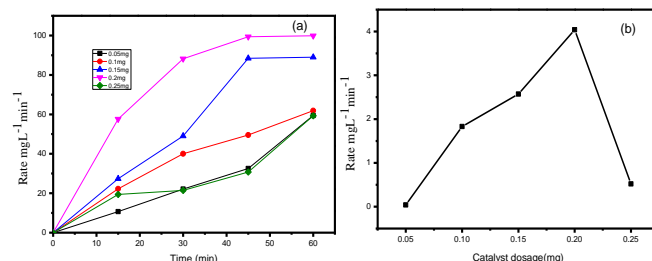
This influences the diminishing of +ve charge of the catalyst surface slowly when the pH going towards the high pH then, the rate of degradation decreases.



**Fig. 9** The effect of pH on the rate of degradation of FG by 0.75 wt% of P<sup>5+</sup> & 0.25 wt% Co<sup>2+</sup> co-doped TiO<sub>2</sub>. Here, catalyst dosage 10 mg and FG 10 mg/L

#### 3.8.3 Effect of Catalyst Dosage

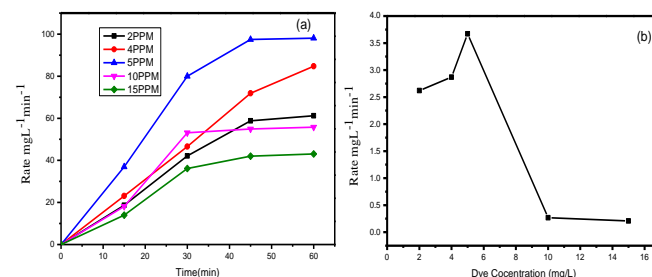
The effect of catalyst dosage on degradation of FG has been given in Figs. 10(a) and (b). The rate of degradation of FG was carried out by varying the catalyst amounts of 25 mg, 50 mg, 100 mg, 150 mg, 200 mg and 250 mg added to 100 mL of solution containing 5 mg/L of dye at pH 2. The rate of degradation increases linearly with the increase of catalyst loading up to 200 mg, further increasing in the catalyst dosage the degradation decreases. This may be due to increase in turbidity, agglomeration of the catalyst particles which restricts the penetration of light transmission to activate the catalyst particles [55]. The collision between active catalyst particles and ground state catalyst particles of co-doped TiO<sub>2</sub> results in deactivation of the catalyst particles [56]. Hence the optimum catalyst dosage found to be 200 mg.



**Fig. 10** Effect of catalyst dosage on the rate of degradation of FG by 0.75 wt% of P<sup>5+</sup> & 0.25 wt% Co<sup>2+</sup> co-doped TiO<sub>2</sub>. Here, pH 2 and FG 10 mg/L

#### 3.8.4 Effect of Initial Concentration of Dye (FG)

To study the effect of initial concentration of dye (FG) at a fixed weight of catalyst 200 mg and at pH 2, experiments were carried out with different concentrations of FG dye from 2 mg/L to 20 mg/L and results are presented in Figs. 11(a) and (b). Results reveals that the rate of degradation of FG dye was very high at 5 mg/L and further increase in dye concentration causes deactivation of the catalyst due to the blanket effect [57].



**Fig. 11** The effect of initial concentration of dye on the rate of degradation of FG. Here, pH 2, catalyst dosage 200 mg

#### 4. Conclusion

P and Co co-doped anatase TiO<sub>2</sub> nano catalysts with small particle size and less band gap energy were successfully synthesized by sol-gel method and characterized by various analytical techniques. In P and Co co-doped TiO<sub>2</sub>, phosphorus causes the shift in absorbance band of TiO<sub>2</sub> from UV to visible region, whereas doping of Cobalt inhibits the electron/hole recombination and acts as charge carrier during photocatalytic degradation. Under visible light irradiation PCT<sub>1</sub> (0.750 wt% of P and 0.25 wt% of Co) Co-doped TiO<sub>2</sub> exhibited high photocatalytic activity compared to other nano catalysts and undoped TiO<sub>2</sub>. Finally the optimum reaction parameters were established for complete degradation of dye Fast Green at 5 mg/L dye was successfully degraded by 200 mg of catalyst (PCT<sub>1</sub>) at pH 2 under visible light irradiation for 60 min.

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