



# Tailored highly efficient Co-doped TiO<sub>2</sub>/CoTiO<sub>3</sub> heterojunction photocatalyst for methylene blue degradation under visible light

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## Abstract

A typical Co-doped TiO<sub>2</sub>/CoTiO<sub>3</sub> heterostructure photocatalyst was synthesized using a facile and cost-effective modified sol–gel route. The as-prepared photocatalysts were further annealed at 400, 600, and 700 °C temperatures and termed CT400, CT600, and CT700, respectively. The XRD analysis of the CT600 photocatalyst reveals the presence of anatase–rutile homojunction and the high crystallinity nature of TiO<sub>2</sub>. The spectral response and the bandgap of the photocatalysts were analyzed using UV-DRS. The decrease in bandgap due to Co ion doping as well as the synergistic effect of both homojunction and heterojunction in Co-TiO<sub>2</sub>/CoTiO<sub>3</sub> significantly enhanced the photocatalytic activity under visible light. The presence of oxygen vacancies, charge carrier migration, and the chemical compositions of the photocatalysts were studied using ESR, PL, and XPS techniques. Under the visible light, Co-TiO<sub>2</sub>/CoTiO<sub>3</sub> (CT600) photocatalyst exhibited 97% degradation of methylene blue in 90 min, which is ~42-fold higher than that of pristine TiO<sub>2</sub>. No sacrificial reagents were applied in this research. Notably, this visible light active Co-TiO<sub>2</sub>/CoTiO<sub>3</sub> photocatalyst has the potential for the application of large-scale solar-induced dye removal.

**Keywords** Photocatalysis · Heterojunction homojunction · Methylene blue · Visible light

## 1 Introduction

Excessive industrial discharges of thiazine-based dyes to water bodies without treatment can jeopardize human and animal lives. Photocatalytic degradation of thiazine dyes using a semiconductor-based photocatalyst is a sustainable and renewable process to mitigate these water pollutants. Photocatalysts with nanoscale materials can be very beneficial owing to their large surface area-to-volume ratio. They are highly active in removing dye-contaminated pollutants from aquatic bodies through a low energy-intensive

process. Methylene blue (MB) is a thiazine-based water pollutant widely used in the fabric, paper, and paint industries [1]. The discharge of huge amounts of MB-contaminated wastewater into the aqueous reservoir threatens the natural ecosystem and must be eliminated before being released into the environment [2]. Metal oxide nanomaterials like TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> have been extensively explored for their potential applications in solar light-driven photocatalysis [1, 3]. Particularly, titanium dioxide (TiO<sub>2</sub>) semiconductor has been intensively focused for various applications among the metal oxide photocatalysts. The fascinating properties of TiO<sub>2</sub>, for instance, super resistive to photocorrosion, suitable energy band positions corresponding to the oxidation–reduction potential, and non-toxicity toward water have drawn significant attention for potential application in H<sub>2</sub> evolution, dye-sensitized solar cells, air purification, and photocatalytic wastewater treatments [4, 5]. In addition, TiO<sub>2</sub> is regarded as an excellent candidate for the redox treatment of numerous organic pollutants under light illumination [6].

However, the pristine and unmodified TiO<sub>2</sub> suffers from poor visible light absorption due to the large bandgap. Besides, the quick recombination of photoexcited electron–hole pairs in pure TiO<sub>2</sub> limits its practical application [7]. By addressing

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the aforementioned issues via strong visible light harvesting and inducing large spatial separation of electron–hole pairs, photocatalytic efficiency could be enhanced. In addition, the existence of mixed-phase homojunction between the polymorphs of  $\text{TiO}_2$  (i.e., anatase and rutile) readily separates the photogenerated charge carriers through interfacial transport processes, resulting in increased photocatalytic activity [3]. Several studies have been reported over the past decades to overcome the limitations of  $\text{TiO}_2$  by doping with anionic and cationic elements [8], dye-sensitization [9], noble metals [10], and composition with other semiconductors [11, 12]. However, most of the previous studies were unsuccessful to deliver excellent photocatalytic performance without using sacrificial agents under the visible range.

The transition metal doping on the host semiconductor can increase the spectral response and reduce the recombination rate [13–15]. Cobalt is regarded as one of the most promising transition metal dopants for enhancing the visible light response of a host semiconductor. Liu et al. reported efficient photoelectrochemical (PEC) water splitting by Co-doped  $\text{TiO}_2$  nanowire arrays integrated on a fluorine-doped tin oxide (FTO) substrate [16]. Recently, Mragui et al. demonstrated excellent methyl orange (MO) conversion using 1% Co-doped  $\text{TiO}_2$  under visible light [17]. However, high concentration transition metal doping often suffers from major setbacks like thermal instability and poor quantum yield of the photocatalytic reactions [7].

The fabrication of heterojunction between different photocatalytic materials is considered a viable method to suppress the photogenerated charge recombination that occurs during swift electron–hole separation through the interfacial junction [18, 19]. The built-in electric field due to energy band mismatch across the junctions promotes the photogenerated charge carrier separation [18]. Zhang et al. demonstrated substantial charge carrier separation and significant visible light response in an n-p-n type heterojunction of  $\text{TiO}_2/\text{Bi}_2\text{O}_3/\text{TiO}_2$  [20]. Recently, coupling  $\text{TiO}_2$  with low bandgap titanium-based typical  $\text{ATiO}_3$  structured perovskite material ( $A = \text{Fe, Pb, Zn, Co, Sr, and Ni}$ ) has drawn significant attention due to their excellent photocatalytic degradation [21–23]. The improved interfacial charge transfers in the perovskite  $\text{ABO}_3$  material within the localized electric field caused by the spontaneous dipole moment enhances the photocatalytic activity [23]. Cobalt titanate ( $\text{CoTiO}_3$ ) is a narrow bandgap perovskite oxide material studied for potential application in magnetic media, electronic noses, and Li-ion batteries [24, 25]. Again,  $\text{CoTiO}_3$  has been reported with high photocatalytic degradation and oxygen evolution activity [26, 27]. Furthermore,  $\text{PtCoFe/MWCNT-TiO}_2$  heterojunction electrocatalyst is reported for efficient methanol oxidation [28]. Recently, Lin et al. illustrated visible light active type II heterojunction among C-TiO<sub>2</sub> and  $\text{CoTiO}_3$  with effective photoactivity and

remarkable reusability in the degradation of ciprofloxacin [29]. Noypha et al. reported a  $\text{Fe}_2\text{O}_3$ -graphene-Ag catalyst that can undergo sonocatalytic activity toward MB [30]. Again, self-recoverable  $\text{ZnS-WO}_3\text{-CoFe}_2\text{O}_4$  nanohybrid photocatalyst was illustrated by the Palanisamy research group; however, their photocatalytic efficiency toward MB was relatively lower compared to our report [31].

In this study, cobalt-doped titania ( $\text{Co-TiO}_2$ ) was synthesized using a cost-effective sol–gel route.  $\text{Co-TiO}_2/\text{CoTiO}_3$  heterojunction with  $\text{TiO}_2$  mixed-phase (anatase–rutile) homojunction was attained via a post-thermal treatment. A  $\text{CoTiO}_3$  perovskite structure was confirmed along with the mixed polymorphs of  $\text{TiO}_2$  using characterization techniques. The coexistence of  $\text{CoTiO}_3$  and  $\text{Co-TiO}_2$  matrix had a synergistic role in enhancing photocatalytic activity under visible light toward MB degradation.

## 2 Experimental

### 2.1 Materials and methodology

The Co-doped  $\text{TiO}_2$  nanoparticles were prepared using titanium (IV) isopropoxide (TTIP, 95%, Alfa Aesar, USA), 2-propanol (99%, Merck, India), cobalt (II) nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 97%, Merck, India) and nitric acid ( $\text{HNO}_3$ , 69%, Merck, India). Initially, a precursor solution was prepared with 40 mL of 2-propanol and 4 mL of TTIP. Subsequently, a specific amount (1 wt % Co) of cobalt compound was mixed with the precursor solution. An hour later, 1 mL of  $\text{HNO}_3$  was poured into the mixture. The solution was then stirred vigorously for the following 24 h and kept for aging till the next 72 h. The remaining moisture was removed by heating and the obtained product was then pulverized into fine powder. The obtained sample was then annealed at 400, 600, and 700 °C for two hours and denoted as CT400, CT600, and CT700. The graphical illustration of the synthesis procedure is provided in Fig. S1 (SI).

For the preparation of pure  $\text{TiO}_2$ , initially, 40 mL of isopropanol was taken in a beaker and then 4 mL of TTIP was poured dropwise and homogenized. Subsequently, after 30 min, 1 mL of  $\text{HNO}_3$  was added. This solution mixture was continuously stirred for the following 24 h and further aged for another 72 h to get a gel form. The gel was then heated to eliminate any leftover moisture before being grounded into a fine powder. The as-prepared sample was then annealed at 400 °C and termed as a T400 photocatalyst.

### 2.2 Sample characterizations

The crystallinity and structural phases of the synthesized photocatalysts were studied using an X-ray diffractometer

(Bruker AXS, D8-Advance, Germany, equipped with Cu K $\alpha$  wavelength  $\lambda = 1.54 \text{ \AA}$ ). The Optical absorbance spectra of the photocatalysts were recorded in a UV–visible diffuse reflectance spectrophotometer (Shimadzu, UV2600, Japan). The structural morphology of the photocatalysts was determined using a scanning electron microscope (SEM, JSM-6390L, JEOL, Japan) and transmission electron microscope (TEM, FEI, TecnaiG2 F20, S-twin, USA). In addition, the presence of the specific elements in a catalyst was ensured by energy-dispersive X-ray spectra analysis (EDAX, JSM-6390L, JEOL, Japan). The presence of oxygen vacancies was identified using an electron spin resonance (ESR) spectrometer (JEOL, JSE-FA200, Japan). The photoluminescence spectra were recorded using a fluorescence spectrophotometer (Perkin Elmer, LS-55, USA). The photoelectrochemical (PEC) measurements of the photocatalysts were obtained using a Metrohm-Autolab (PGSTATE-302N, Netherlands). A Thermo Scientific X-ray photoelectron spectrometer (XPS; K-Alpha, Thermo Fisher, UK) was used for analyzing the chemical compositions and the electronic state of the photocatalyst. The XPS spectra were deconvoluted and fitted with XPSPEAK (4.1) software.

### 2.3 Photocatalytic activity evaluation experiment

The photocatalytic test of the as-synthesized catalysts was examined using methylene blue degradation (MB, 82%, Loba Chemie Pvt. Ltd) under visible light. Initially, a 20 mg photocatalyst was loaded in 40 mL of 0.012 mM MB solution and allowed to attain an absorption–desorption equilibrium in the dark for an hour. Subsequently, the above catalyst-loaded suspension was sonicated in an ultrasonicator bath for 1 min and then illuminated by the visible light source (Sansi LED bulb, China,  $\lambda \geq 400 \text{ nm}$ , intensity:  $46.1 \text{ W m}^{-2}$ ) inside a photocatalytic reactor chamber. The suspension was kept under a constant stirring condition throughout the experiment. Afterwards, the MB solution was collected at 15 min intervals. Finally, the collected MB solutions were centrifuged, and the absorption spectra were analyzed using a spectrophotometer (400–700 nm) (make: Shimadzu, model: UV1900).

## 3 Results and discussion

### 3.1 XRD analysis

X-ray diffraction profiles of the photocatalysts T400, CT400, CT600, and CT700 are presented in Fig. 1. The JCPDS reference of TiO<sub>2</sub> for both the anatase and rutile phases, corresponding to PDF no: 89-4921 and 89-4920, are shown in the figure. The observed peaks at  $2\theta = 25.5^\circ, 37.7^\circ, 48.12^\circ, 53.8^\circ, 55.3^\circ, 62.6^\circ$ , and  $75.3^\circ$  in T400 and CT400 are

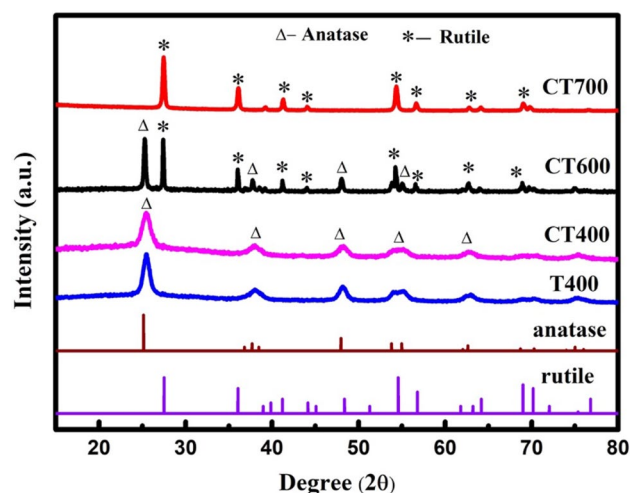


Fig. 1 X-ray diffraction spectra of T400, CT400, CT600, and CT700

ascribed to the anatase structure of TiO<sub>2</sub>, which are related to the (101), (004), (200), (105), (211), (204), and (215) planes, respectively. No diffraction peak was observed for the rutile phase in the T400 and CT400. However, the peak corresponding to the rutile phase appeared at higher calcination temperatures. XRD peaks at  $25.3^\circ, 37.7^\circ, 48.2^\circ, 53.8^\circ, 55.1^\circ, 62.6^\circ, 75.2^\circ$ , and  $2\theta = 27.2^\circ, 36.3^\circ, 41.1^\circ, 54.4^\circ, 56.6^\circ, 64.2^\circ, 69.1^\circ, 69.9^\circ$  in CT600 photocatalyst are due to the anatase and rutile phase [32]. Their reflection planes corresponding to the rutile diffraction peaks are (110), (101), (111), (211), (220), (310), (301), and (112). On the other hand, CT700 sample exhibited only the rutile phase of TiO<sub>2</sub>.

A similar result of temperature-dependent phase transformation was obtained for pristine TiO<sub>2</sub> that was calcined at 600 and 700 °C, and their diffraction patterns are shown in Fig. S2 in SI. The excess interface defects at the anatase grains act as a nucleation site for the growth of the rutile phase when the calcination temperature is increased. During the calcination of the anatase grains at a higher temperature, the interface defects are removed and undergo an interface nucleation process with different arrangements of atoms in the basic TiO<sub>6</sub> octahedra to facilitate the formation of the rutile phase [33, 34]. XRD peak of Co and CoTiO<sub>3</sub> phase was not detected in the diffraction spectra due to the low doping concentration. However, the diffraction peaks of the CoTiO<sub>3</sub> structure were observed (Fig. S3 of SI) on increasing the Co concentration. The crystallite size of TiO<sub>2</sub> was calculated using Scherrer's relation:  $d = K_{ds} \lambda / \beta \cos \theta$ , where  $d$  is the crystallite size,  $K_{ds}$  is the shape factor (0.9),  $\lambda$  is the wavelength of the X-ray,  $\beta$  is the FWHM, and  $\theta$  is the Bragg angle [25]. The calculated  $d$  value of T400 and CT400 was  $\sim 11$  and  $\sim 10$  nm. The crystal sizes are found to increase with increasing annealing temperature (Shown in Table 1).

**Table 1** Bandgap and crystallite size of the as-prepared photocatalysts

| Photocatalyst | Bandgap (eV)     | Crystallite size (nm) |
|---------------|------------------|-----------------------|
| T400          | 3.24             | ~ 11                  |
| CT400         | 3.08, 2.44, 1.54 | ~ 10                  |
| CT600         | 3.01, 2.45, 1.64 | ~ 25                  |
| CT700         | 2.90, 2.33, 1.85 | ~ 29                  |

These relatively smaller sizes of nano-photocatalysts can induce higher electron transfer within a specific light range.

### 3.2 UV–visible diffusion reflectance spectra analysis

Absorbance spectra of T400, CT400, CT600, and CT700 in the UV–visible region are shown in Fig. 2a. A sharp spectral absorption corresponding to the primary energy band transitions of  $\text{TiO}_2$  was observed in the ultraviolet region (around

380 nm) in the pristine  $\text{TiO}_2$  [19]. The broad nature of the absorbance spectrum in Co-doped  $\text{TiO}_2$  (CT400) with a slight red-shift compared to the pure  $\text{TiO}_2$  (T400) was noticed. The absorbance spectra were further shifted toward higher wavelengths in the CT600 and CT700. These red-shifts in the optical absorption were ascribed to the bandgap reduction as a consequence of the interaction between free  $sp$ -electrons and localized  $d$ -electrons of Co ions [35]. In addition, strong spectral absorption in the range of 500–750 nm was detected in both the CT600 and CT700 photocatalyst, which is related to the characteristic absorption band of the  $\text{CoTiO}_3$  phase arising due to  $\text{Co}^{2+}$  to  $\text{Ti}^{4+}$  charge transfer interaction [36]. However, this wide-range spectral response was decreased significantly in CT700, ascribing the dominance of rutile structure at high calcination temperature.

To calculate the bandgap of the materials, the Kubelka–Munk (K–M) function  $F(R)$  was initially obtained from the diffuse reflectance data  $R\%$  using Eq. (1) [35]:

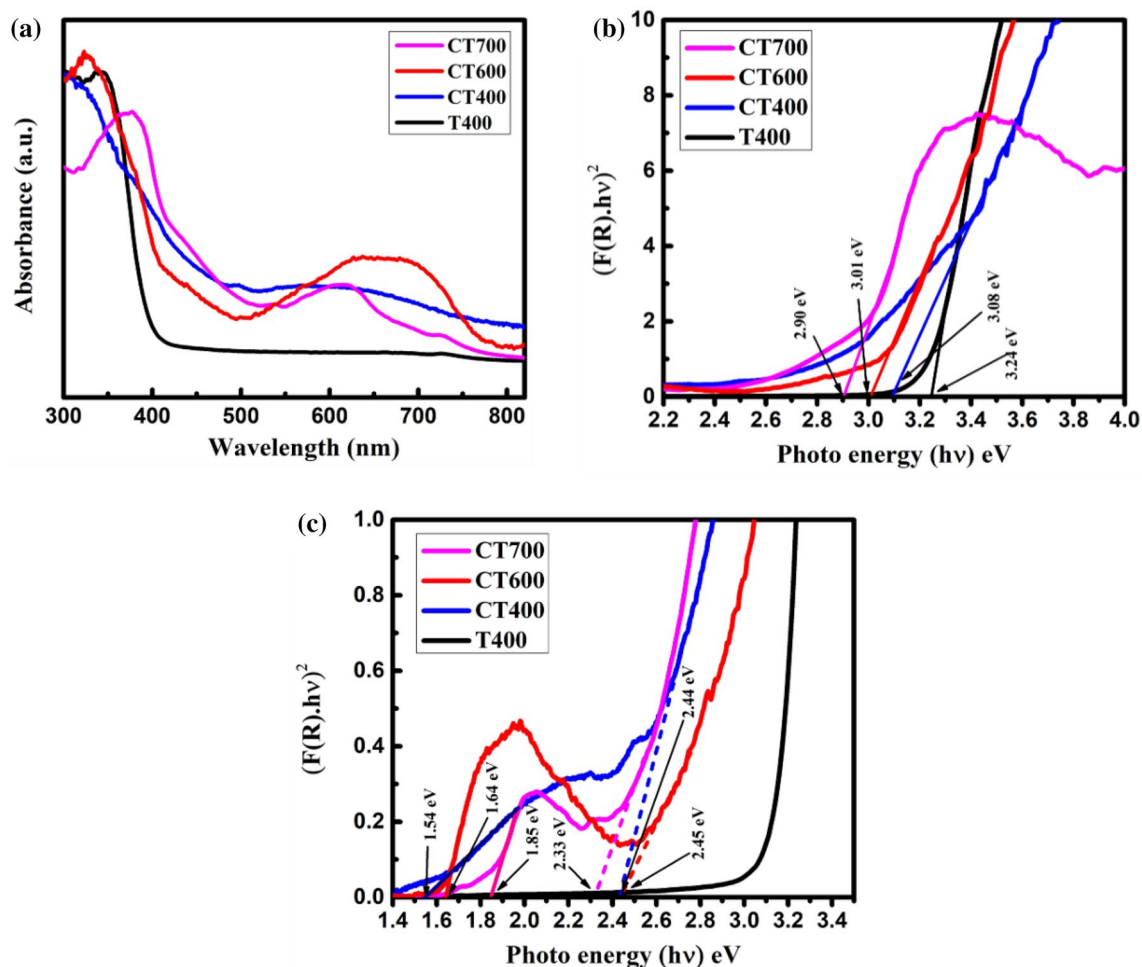


**Fig. 2** a Optical absorbance spectra, b bandgap determination, and c Magnified y-axis data of T400, CT400, CT600, and CT700 photocatalysts

$$F(R) = \frac{(1-R)^2}{2R} \quad (1)$$

The Tauc's relation between the bandgap of a semiconductor and the optical absorption coefficient is given by Eq. (2).

$$(\alpha \cdot h\nu) = A(h\nu - E_g)^n \quad (2)$$

where  $A$  is a proportionality constant,  $\alpha$  is the extinction coefficient,  $E_g$  is the bandgap of the semiconductor,  $n$  is an integer,  $\nu$  is the frequency of incoming waves, and  $h$  is the Planck's constant [37]. The integer  $n$  is calculated by the type of optical transitions and the typical values are  $n = \frac{1}{2}$  and  $n = 2$  for the direct and indirect band transition. Since the transformed K–M function  $F(R)$  is directly related to the extinction coefficient, the bandgap of the materials can be calculated using the following relation [38]:

$$(F(R) \cdot h\nu) = A(h\nu - E_g)^n \quad (3)$$

The value of  $n$  was calculated to understand the nature of optical transitions in the material. The following equation can be obtained by taking the logarithm of Eq. (2) [39].

$$\ln(\alpha \cdot h\nu) = \ln A + n \ln(h\nu - E_g) \quad (4)$$

By plotting  $\ln(h\nu - E_g)$  vs.  $\ln(\alpha \cdot h\nu)$  graph, the slope  $n$  was obtained to be  $\sim 0.5$  for all the photocatalysts (shown in Fig. S4 in SI), which suggests the direct band transition ( $n = 1/2$ ) of the materials. Accordingly, the bandgap values of all the materials were obtained by extrapolating the absorption band to the  $h\nu$  axis from the  $(h\nu \text{ vs. } (F(R) \cdot h\nu)^2)$  graph (shown in Fig. 2b). The bandgap of the pristine T400 was found to be  $\sim 3.24$  eV that concurs to the electronic transition between the primary energy bands of the anatase phase of titania.

The bandgap of CT400, CT600, and CT700 photocatalysts is reduced to 3.08, 3.01, and 2.90 eV. This bandgap reduction was due to the formation of defect sites in the forbidden locality of titania by  $\text{Co}^{2+}$  ion substitution in the  $\text{TiO}_2$  matrix [35, 40]. Notably, two additional bandgaps were obtained for each cobalt-doped titania CT400, CT600, and CT700, shown in Fig. 2c (enlarged scale of Fig. 2b). The bandgap values are mentioned in Table 1. The bandgap of CT400, CT600, and CT700 was estimated to be 2.44, 2.45, and 2.33 eV, which were related to the  $\text{CoTiO}_3$  phase arising due to the  $\text{Co}^{2+} \rightarrow \text{Ti}^{4+}$  charge transfer (octahedral coordination  $\text{Co}^{2+}$ ) [41]. Additionally, the optical transitions corresponding to the bandgap 1.54, 1.64, and 1.85 eV are associated with the  $^4\text{A}_2(\text{F})$  to  $^4\text{T}_1(\text{P})$  transition in the tetrahedrally coordinated  $\text{Co}^{2+}$  or  $\text{Co}^{3+}$  [35]. The above results and discussion indicate the formation of the Co-doped  $\text{TiO}_2$  and  $\text{CoTiO}_3$  phases in the matrix ( $\text{Co-TiO}_2/\text{CoTiO}_3$ ). The narrow  $\text{TiO}_2$  bandgap occurred due to Co doping improved visible light absorption,

and the interfacial junctions minimized the recombination rate and prolonged the charge carriers for photocatalytic reactions.

### 3.3 SEM and TEM analysis

SEM images were examined to understand the morphological structure of the photocatalysts. Figure 3a, b depict the SEM images of pristine titania T400 and Co-doped titania CT600. The homogeneous distribution having average particle sizes of  $\sim 20$  and  $\sim 23$  nm for T400 and CT600, respectively, that was confirmed using ImageJ software. Figure 3c, d represent the EDX spectra of the T400 and CT600 photocatalysts with their atomic compositions. EDX results confirmed the existence of Ti, O, and Co in the CT600 sample. Both T400 and CT600 photocatalysts exhibited mesoporous structures with no major aggregation of larger-size clusters.

To study the particle size distribution and microstructure of the photocatalysts, the TEM and HR-TEM images are analyzed. Figure 4a, b and Fig. 4c, d depict the TEM and HR-TEM images of T400 and CT600, respectively. The particle size homogeneity in T400 and CT600 was evident in Fig. 4a, c. The interplanar  $d$ -spacing of T400 was calculated to be  $3.4 \text{ \AA}$ , which is the typical value of the anatase phase of  $\text{TiO}_2$  (Fig. 4b). The HR-TEM image of CT600 shows the  $d$ -spacing value of the anatase and rutile phases that correspond to  $3.4 \text{ \AA}$  and  $3.2 \text{ \AA}$  (shown in Fig. 4d). Besides, CT600 exhibits an additional interplanar gap of  $d = 2.7 \text{ \AA}$ , which was attributed to the  $\text{CoTiO}_3$  crystal. This result further indicates the coexistence of  $\text{CoTiO}_3$  crystal in the matrix along with the anatase and rutile phases. The selected area electron diffraction (SAED) pattern of the CT600 photocatalyst is presented in Fig. 4e. The concentric rings reveal the polycrystalline nature of the photocatalyst [28]. The  $d$ -spacing (radius calculated from the central spot of the Scherrer's ring) of the anatase phase corresponding to (101) and (200) planes agree with the calculated values from XRD. The concentric rings of (101), (211), and (310) planes are assigned to the  $d$ -spacing of the rutile phase. In addition, the  $d$ -spacing corresponding to the  $\text{CoTiO}_3$  phase was indexed with the ring (104). The mean particle size distribution of  $\text{TiO}_2$  nanoparticles in CT600 was  $\sim 22$  nm (shown in the bar diagram, Fig. 4f).

### 3.4 ESR analysis

Photocatalyst when exposed to light generates electron–hole pairs, which later interacts with  $\text{H}_2\text{O}$  and dissolved oxygen and produces radical like  $\bullet\text{O}_2^-$ ,  $\text{h}^+$ , and  $\text{e}^-$  and completes the redox reaction. The number of free electron and oxygen vacancies within the photocatalyst can be obtained from ESR. Figure 5 shows the ESR results of T400, CT400, and CT600 photocatalysts measured at room temperature. The

**Fig. 3** SEM images of **a** T400 and **b** CT600, along with their magnified view of the selected area. EDX of **c** T400 and **d** CT600 with atomic composition

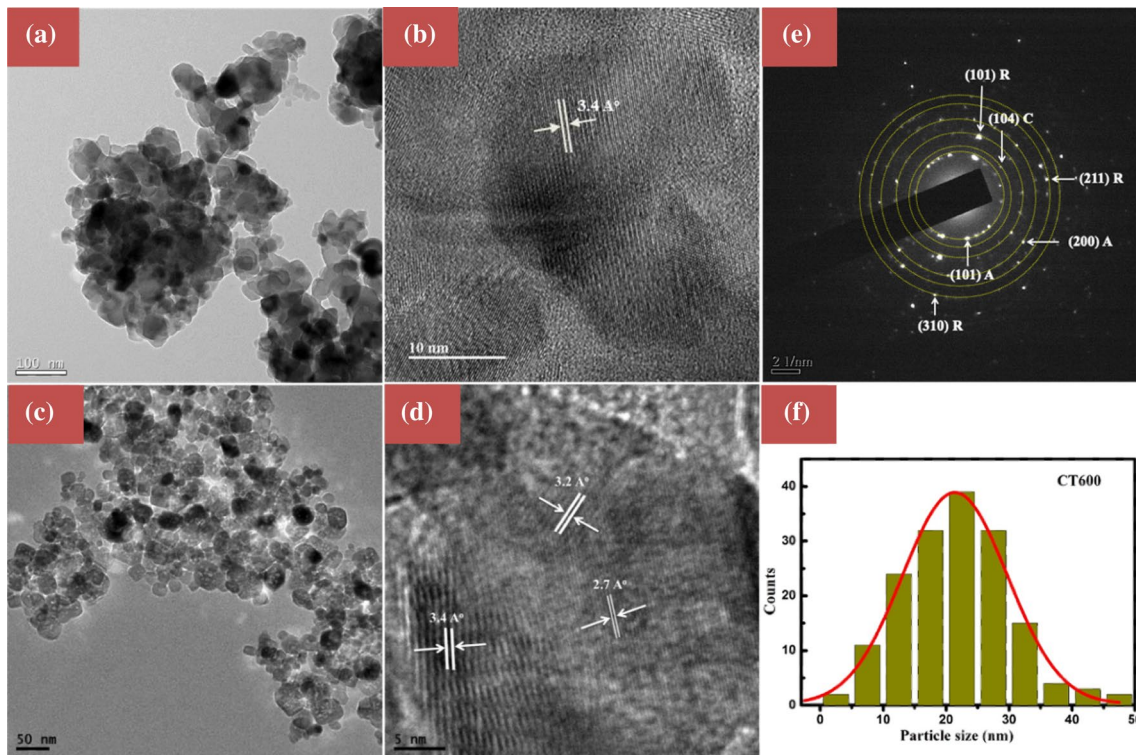
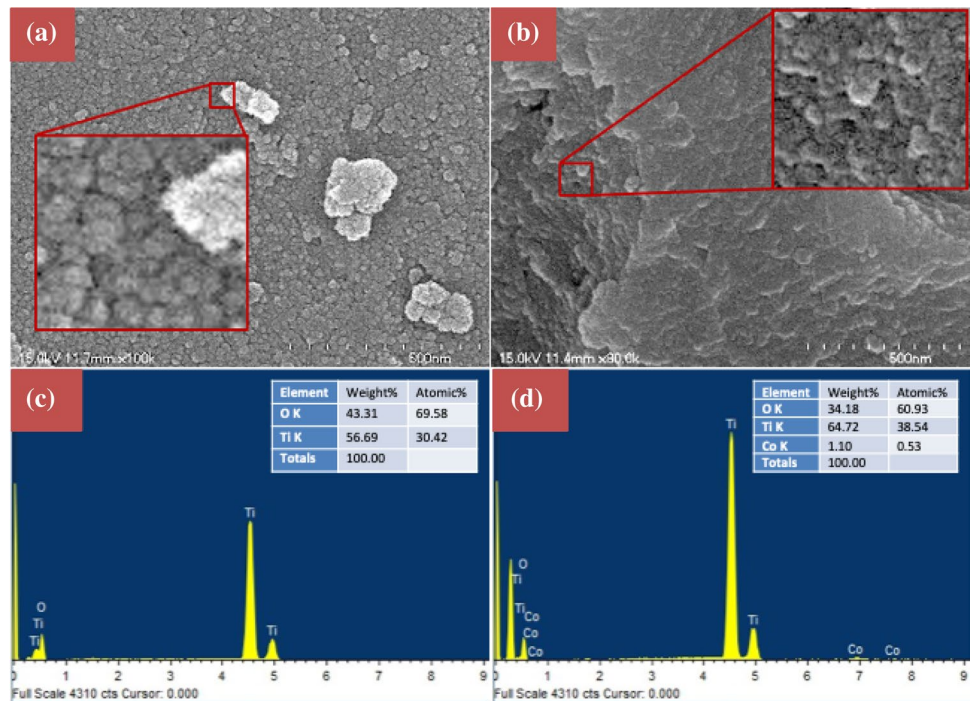


**Fig. 4** TEM and high-resolution TEM **a, b** T400 and **c, d** CT600. **e** SAED pattern with the lattice planes and **f** particle distribution of CT600

Lande  $g$ -factors of the electrons are calculated from  $g = h\nu/\beta H_o$ , where  $h$ ,  $\nu$ ,  $\beta$ , and  $H_o$  are the Planck constant,

frequency, Bohr magneton, and resonance magnetic field, respectively [42]. The broad anisotropic resonance peak observed at  $g=2.06$  and  $2.03$  in T400 and CT400 is assigned

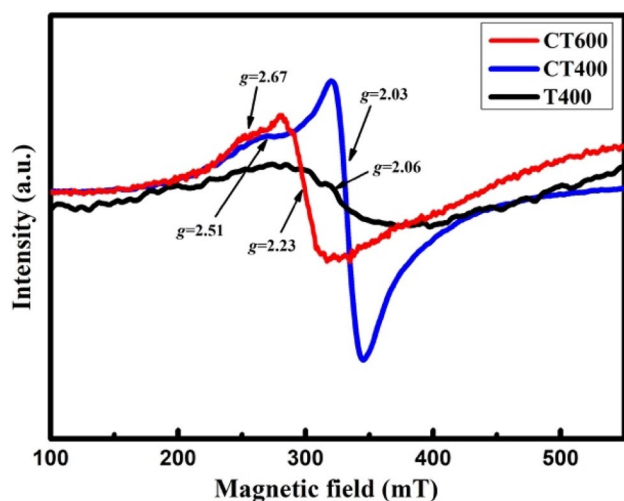


**Fig. 5** ESR spectra of T400, CT400, and CT600 photocatalysts at room temperature

to the surface  $\text{Ti}^{3+}$ , where the atmospheric  $\text{O}_2$  gets adsorbed and consequently reduces to  $\text{O}^{2-}$  [43].

The ESR peak intensity was significantly increased after Co incorporation in  $\text{TiO}_2$ , which signifies the creation of more  $\text{Ti}^{3+}$  species. The ESR resonance signal at  $g=2.23$  in the CT600 was due to the  $\text{Co}^{2+}$  ions combined with oxygen vacancies in an octahedral site of  $\text{CoTiO}_3$  [43, 44]. Besides, a hump of ESR peak was seen at  $g=2.51$  in CT400 and  $g=2.67$  in CT600, which was due to the tetrahedrally coordinated high spin state of  $\text{Co}^{2+}$  ions [35, 44].

### 3.5 Photoluminescence spectra analysis

Photoluminescence (PL) spectroscopy is a useful technique to investigate the band transition, migration, and recombination of the photogenerated charge carriers. Figure 6 shows the room temperature PL spectra of T400, CT400, and CT600 photocatalysts at an excitation wavelength of 320 nm. The emission peak at 385 nm in T400 is ascribed to  $\text{TiO}_2$  onset band transitions with a band gap of  $\sim 3.2$  eV. The PL intensity was observed to be quenched in both the photocatalyst CT400 and CT600, indicating the lower recombination rate of the photogenerated charge carriers. The PL peaks at 436 and 451 nm in CT400 and CT600 are corresponding to the defect state transitions due to  $\text{Co}^{2+}$  ion substitution in the  $\text{TiO}_2$  matrix [35]. The low-intensity emission peaks at around 477 nm correspond to the self-trapped excitons generated due to the transition from  $\text{Ti}^{3+}$  3d states to the deep acceptor levels near the valence band maximum [45, 46]. The emission at 518 nm corresponding to an energy gap of  $\sim 2.4$  eV arose due to the transition from lower level of oxygen vacancies to the ground state [46].

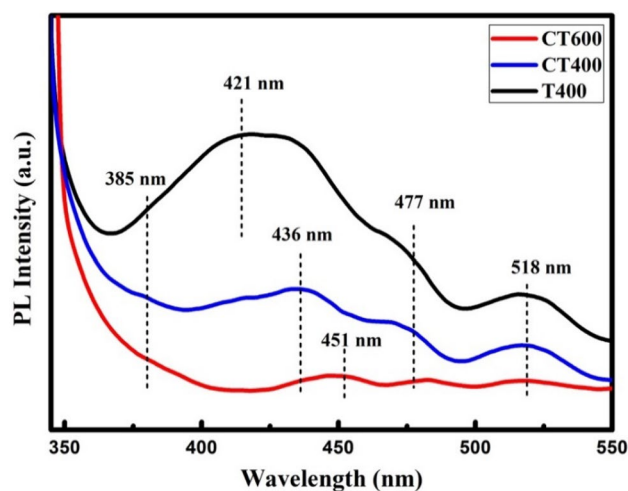


**Fig. 6** Photoluminescence spectra of T400, CT400, and CT600 photocatalysts at room temperature

### 3.6 XPS study

The oxidation state and chemical compositions on the surface of the prepared photocatalyst were studied using XPS. The full survey spectra of T400, CT400, and CT600 are shown in Fig. S5a. The presence of Ti, O, and Co on the surface was confirmed in CT400 and CT600 catalysts. A peak due to extraneous carbon contaminant was observed at the binding energy (BE) 285.5 eV [47], which may be due to the carbon compound adhered to the surface of photocatalysts. XPS spectra of Ti 2p and O 1s for T400, CT400, and CT600 are presented in Fig. S5b and S5c of SI. The O1s peaks are found to be slightly shifted toward higher binding energies in Co-doped  $\text{TiO}_2$ . The high-resolution Ti spectra of T400 reveal the  $\text{Ti}^{4+}$  state with two prominent peaks at BE 458.2 and 464.0 eV, corresponding to Ti ( $2p_{3/2}$ ) and Ti ( $2p_{1/2}$ ) doublets [48]. After Co doping, the Ti 2p peaks are shifted toward higher BE by  $\sim 0.3$  and  $\sim 0.6$  eV in CT400 and CT600, respectively.

The positive shift observed in the binding energy values of O1s peaks of CT400 and CT600 in comparison to T400 indicates the lower electron density of oxygen species of  $\text{TiO}_2$  in CT400 and CT600 than that of T400 [49]. Again, the positive shifts observed in the binding energy values of Ti 2p peaks of CT400 and CT600 in comparison to T400 suggest the presence of higher electron density at Ti sites. This implies the existence of surface defects because of Co doping in CT400 and CT600, which in turn reduces the Fermi level [49–51]. However, the Ti 2p doublet is separated by 5.8 eV which resembles the standard value of  $\text{TiO}_2$  [52, 53]. The peak location of Ti ( $2p_{3/2}$ ) and Ti ( $2p_{1/2}$ ) doublet is 458.5 and 464.3 eV in CT400, whereas, for CT600, the peaks are shifted to 458.8 and 464.6 eV.

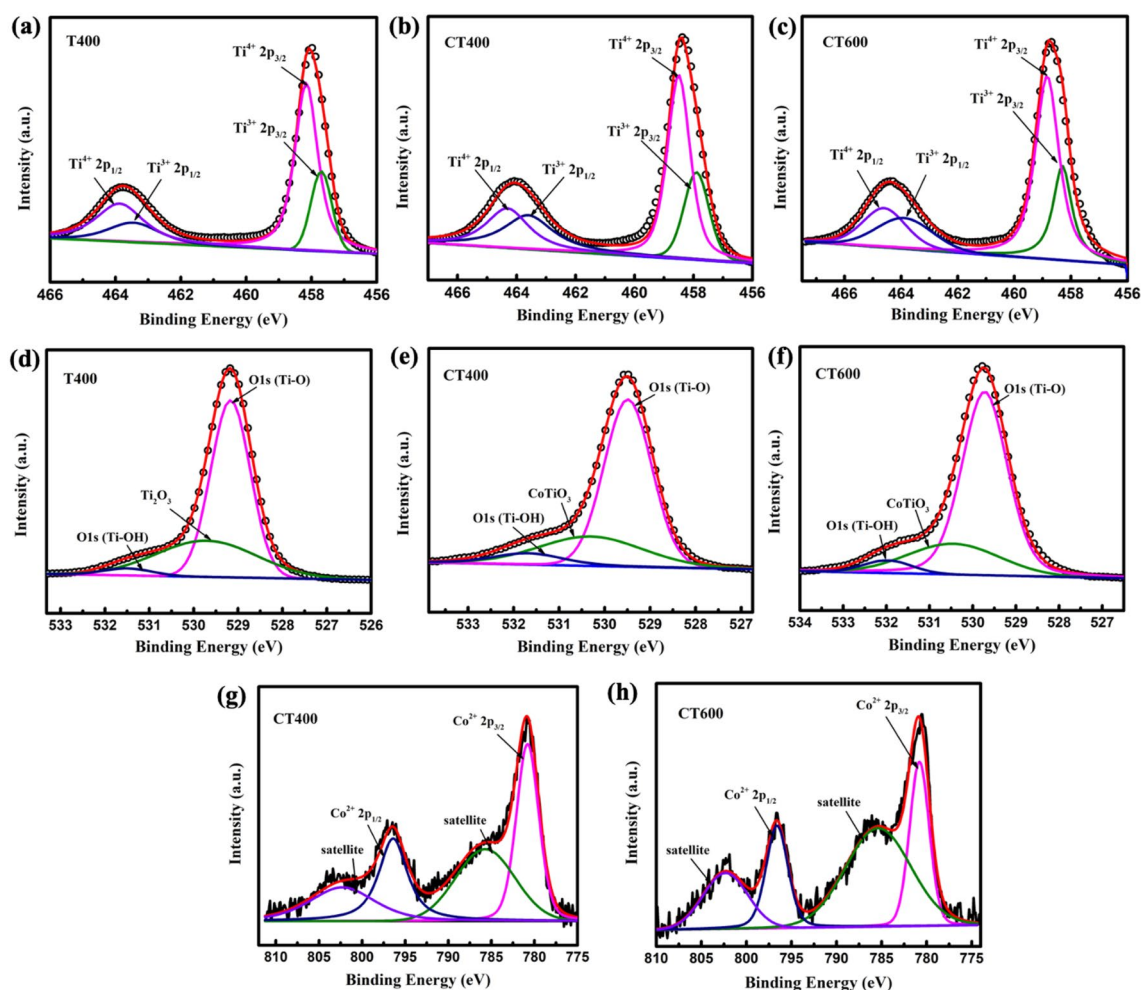


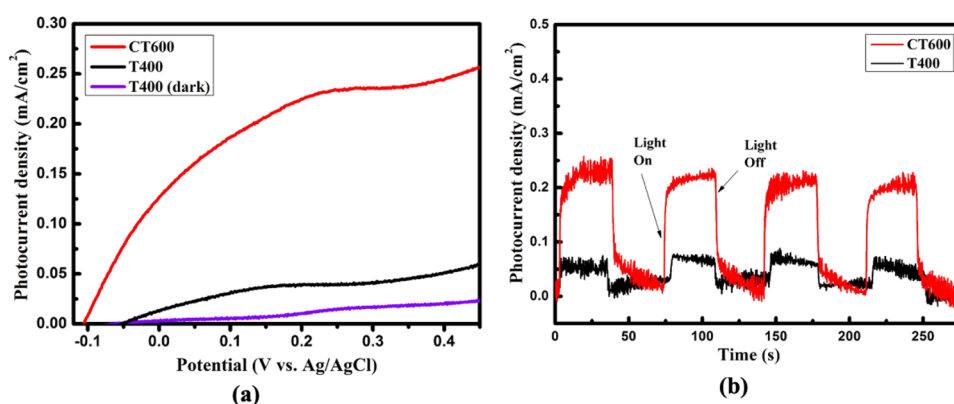
**Fig. 7** XPS peak fitting: Ti 2p spectrum of **a** T400, **b** CT400 and **c** CT600. O1s spectra of **d** T400, **e** CT400 and **f** CT600. Co 2p spectra of **g** CT400 and **h** CT600

For T400, the Ti 2p spectrum was deconvoluted into four peaks at 457.7, 458.2, 463.5, and 464.0 eV (shown in Fig. 7a). The shoulder peaks at 457.7 and 463.5 eV correspond to the  $\text{Ti}^{3+}$  ( $2p_{3/2}$ ) and  $\text{Ti}^{3+}$  ( $2p_{1/2}$ ), respectively. Likewise, the Ti 2p spectra in Co incorporated catalysts were deconvoluted into four peaks. They were positioned at 457.8, 458.5, 463.6, and 464.3 eV for CT400 (Fig. 7b); and 458.2, 458.8, 464.0, and 464.6 eV for CT600 (Fig. 7c). The deconvoluted peaks at 457.8 and 463.6 eV in CT400, and 458.2 and 464.0 eV in CT600 are ascribed to the  $\text{Ti}^{3+}$   $2p_{3/2}$  and  $\text{Ti}^{3+}$   $2p_{1/2}$  states, respectively [51, 54]. The XPS peak area related to  $\text{Ti}^{3+}$   $2p_{3/2}$  was increased by  $\sim 7$  and  $\sim 21\%$  in CT400 and CT600 compared to the pristine T400 photocatalyst. In addition, the XPS peak area corresponding to  $\text{Ti}^{3+}$   $2p_{1/2}$  is found to be increased by  $\sim 47$  and  $\sim 12\%$  in CT400 and CT600 compared to the pristine T400. Consequently, the area of the peak corresponding to  $\text{Ti}^{4+}$   $2p_{1/2}$ , and  $\text{Ti}^{4+}$   $2p_{3/2}$  decreased significantly in both the CT400 and CT600. This indicated the generation of more oxygen vacancies after Co

incorporation in  $\text{TiO}_2$ , which agrees with the ESR analysis. The deconvoluted XPS peak areas of the photocatalysts are presented in Table ST1 in SI.

The high-resolution O1s XPS peaks of pristine  $\text{TiO}_2$  (T400) located at the BE 529.2 and 531.5 eV are imputable to the lattice-oxygens (Ti–O) and the bridging hydroxyl groups (Ti–OH) on the surface, respectively (shown in Fig. S5c) [51]. A slight positive shift in the BE positions of the O1s peaks is observed at 529.4 and 531.7 eV for CT400; and 529.7 and 532.0 eV for CT600. The broad O1s XPS peaks can be deconvoluted into three peaks with the BE positions 529.2, 529.7, and 531.5 eV for T400 (Fig. 7d); 529.4, 530.3, and 531.7 eV for CT400 (Fig. 7e); and 529.7, 530.4, and 532.0 eV for CT600 (Fig. 7f). The well-fitted XPS spectra at BE 529.7, 530.3, and 530.4 eV in T400, CT400, and CT600, respectively, were related to the formation of  $\text{Ti}_2\text{O}_3$  and  $\text{CoTiO}_3$  in the matrix [55]. The slight reduction in the XPS peak area of  $\text{Ti}_2\text{O}_3$  in CT400 and CT600 indicates the formation of  $\text{CoTiO}_3$ .

**Fig. 8** **a** Current–voltage (I–V) characteristics of T400 and CT400. **b** Chronoamperometric current of T400 and CT600 sample recorded at 0.4 V (vs. Ag/AgCl)



The well-resolved spectra of Co 2p of cobalt-doped CT400 and CT600 are in Fig. S5d of SI. The XPS peak at the BE 780.7 and 796.4 eV in CT400 is ascribed to the Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> core level transitions, respectively. The strong satellite peaks at 785.7 and 802.2 eV reveal the presence of a high spin Co<sup>2+</sup> state in the TiO<sub>2</sub> matrix and the formation of mixed metal oxides (CoTiO<sub>3</sub>) [51]. The XPS core level and satellite peaks in CT600 are located at BE 780.8 (Co 2p<sub>3/2</sub>), 785.4 (satellite), 796.6 (Co 2p<sub>1/2</sub>), and 802.3 (satellite) eV. The well-resolved deconvoluted Co 2p spectra of CT400 and CT600 are shown in Fig. 7g, h. The area of the satellite peaks at BE 785.4 and 802.3 eV is found to be significantly increased by 74% and 55% in CT600 compared to CT400.

### 3.7 Photoelectrochemical (PEC) measurements

The photoelectrochemical measurements were carried out in a three-electrode system electrochemical cell containing 1M NaOH electrolyte with the photocatalyst (deposited on FTO) as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. Figure 8a displays the current–voltage (I–V) characteristics of T400 and CT600. No significant current was obtained under the dark condition in T400. However, under light illumination, the photocurrent density of T400 varies with the increasing electrode potential, while the photocurrent density of the CT600 photocatalyst increases significantly with the increasing bias potential. The CT600 photocatalyst shows more negative open circuit voltage ( $V_{OC}$ ) than T400, indicating the higher charge carrier accumulation and electron–hole separation between the CoTiO<sub>3</sub>/TiO<sub>2</sub> heterojunctions [56]. This result suggests that the Fermi level shifts to more negative potential in the CT400 photocatalyst, which agrees with the XPS result [57].

The chronoamperometric current at 0.4 V (vs. Ag/AgCl) was measured to obtain the photocurrent density of T400 and CT600 photocatalysts and is shown in Fig. 8b. The CT600 photocatalyst exhibited ~0.25 mA cm<sup>-2</sup> photocurrent density, which is 4.6 times than the pristine

T400 (0.05 mA cm<sup>-2</sup>). To evaluate the charge transport characteristics of T400 and CT600 photocatalyst, the electrochemical impedance spectroscopy (EIS) measurements were obtained, shown in Fig. S7 of SI.

### 3.8 Kinetic study for degradation of MB

Figure 9a shows the degradation trend of MB from 0 to 90 min using synthesized photocatalysts under visible light illumination. For reference, control experiments were carried out with fresh MB and pristine TiO<sub>2</sub>. The MB dye degradation was confirmed from the absorbance spectra of the reactant solution. CT600 photocatalyst showed a rapid degradation compared to its counterparts. It was found that the photocatalysts T400, CT400, CT600, and CT700 reduced the initial MB concentration by ~7, 56, 97, and 31% respectively. The optical density spectra of MB dye degradation are displayed in Fig. S6 in SI. The MB degradation trend shown by the photocatalysts revealed that the maximum photocatalytic efficiency could be achieved by increasing calcination temperature up to 600 °C. This is due to the mixed phase of TiO<sub>2</sub> at 600 °C, where the homojunction between anatase and rutile provides more interfacial charge carrier transfer, which eventually minimizes the recombination rate [58].

The rate constant ( $k$ ) of MB degradation was obtained from the linear fitting of  $\ln(C/C_0)$ -time plot, displayed in Fig. 9b. The CT600 photocatalyst shows ~42 times higher degradation rate than the pristine TiO<sub>2</sub> (T400). This enhancement in the activity can be ascribed to (i) intermediate energy states due to Co<sup>2+</sup> doping (bandgap reduction), (ii) homojunction between the anatase and rutile phase, and (iii) heterojunction between TiO<sub>2</sub> and CoTiO<sub>3</sub>. Table 2 displays the rate constant of MB degradation using various photocatalysts. A slight improvement in the photocatalytic activity of CT400 and CT700 compared to pure TiO<sub>2</sub> was also observed, which could be ascribed to the light absorption due to Co<sup>2+</sup> → Ti<sup>4+</sup> charge transfer bands [36, 37]. The absence of homojunction in CT400 and CT700 accounts for the low degradation rate. The optical images of MB

**Fig. 9** **a** Photocatalytic degradation profile ( $C/C_0$  vs. time) of MB under visible light (0–90 min) using T400, CT400, CT600, and CT700 photocatalysts. **b**  $\ln(C/C_0)$  vs. time ( $T$ ) plot to measure the rate constant, **c** Optical images of MB degradation using T400, CT400, CT600, and CT700 photocatalysts, after visible light exposure for 90 min

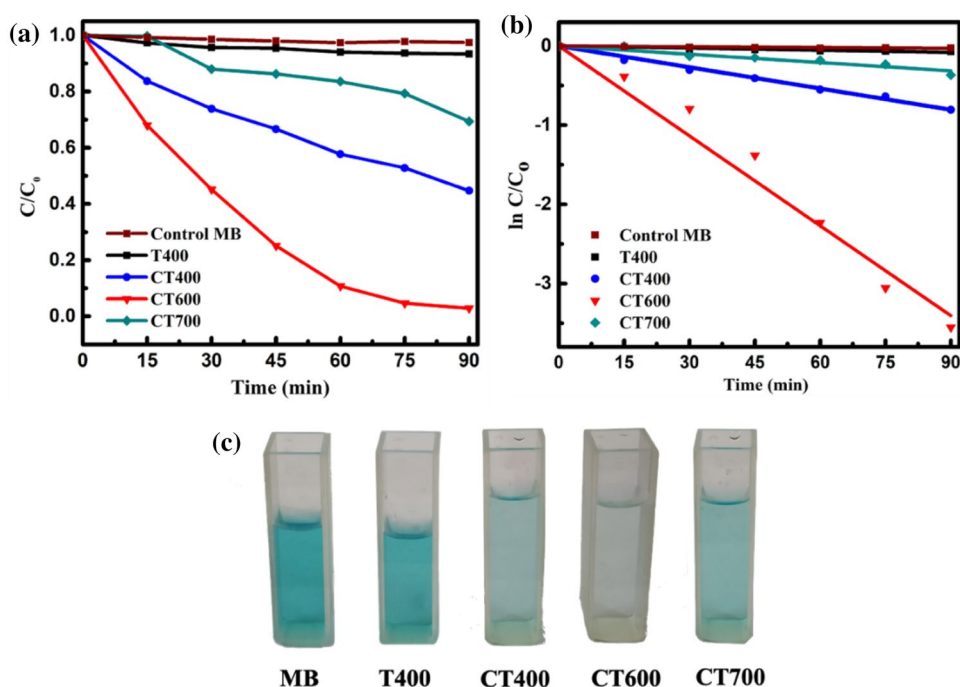


**Table 2** Rate constant of MB degradation using various photocatalyst

| Catalyst | Rate constant ( $k$ ) $\text{min}^{-1}$ |
|----------|-----------------------------------------|
| T400     | 0.0009                                  |
| CT400    | 0.0089                                  |
| T600     | 0.01                                    |
| CT600    | 0.0378                                  |
| T700     | 0.0085                                  |
| CT700    | 0.0035                                  |

degradation of T400, CT400, CT600, and CT700 photocatalysts are shown in Fig. 9c.

Figure 10a illustrates the degradation of MB with illumination time ( $\frac{C}{C_0}$  vs.  $T$ ) by the T600 and T700 photocatalysts.

Their rate constant determination is shown in Fig. 10b. The existence of mixed polymorphs in T600 (as confirmed by XRD analysis, Fig. S2) results in a slight enhancement (1.2 times) in the photocatalytic activity over the T700 photocatalyst. Table ST2 (in SI) summarizes the comparative study of the photocatalytic activity of previously reported photocatalysts. From the table, it is evident that the CT600 photocatalyst demonstrated better photocatalytic output under visible spectra than the other reported photocatalysts. The electron transfer of CT600 was very fast and had a robust and stable structure; therefore, this photocatalyst can be used as an electrocatalyst for water splitting and fuel cells. To study the charge carrier transfer properties, the electrochemical impedance spectra of CT600 and T400 were analyzed. It is known that the larger diameter of the semicircles indicates the higher charge carrier transfer resistance on the related interface [59, 60]. From Fig. S7, it is evident that

**Fig. 10** **a** Photocatalytic degradation profile ( $C/C_0$  vs. time) of MB using T600 and T700 and **b**  $\ln(C/C_0)$  vs. time plot to measure the rate constant

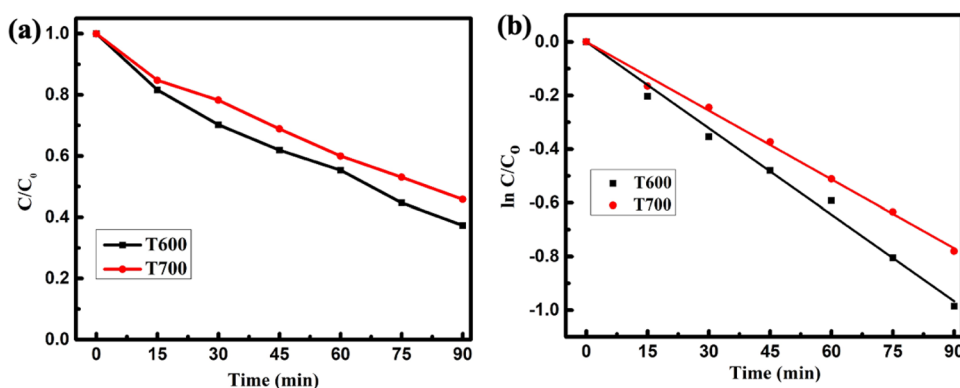
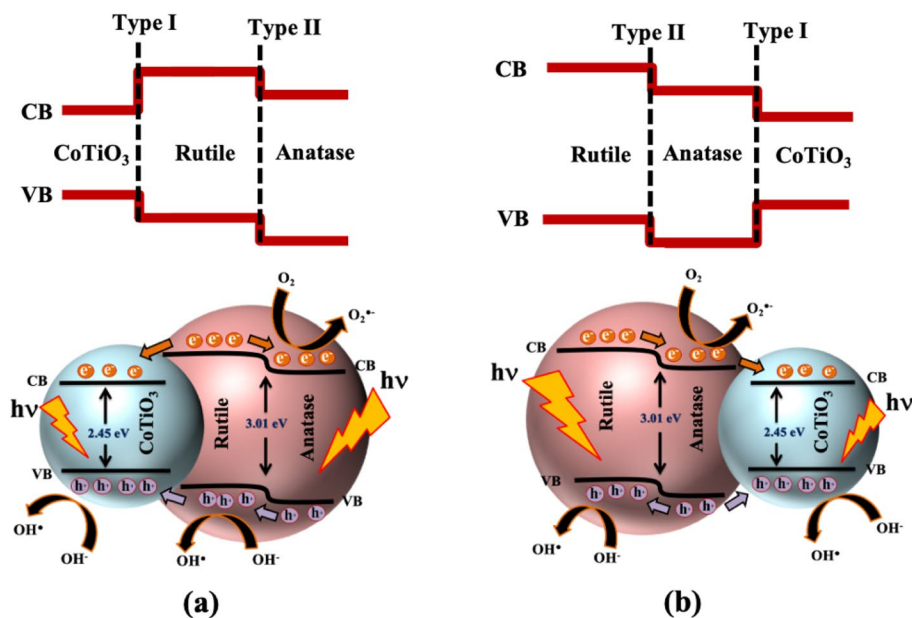


**Fig. 11** Photocatalytic mechanism of Co-TiO<sub>2</sub>/CoTiO<sub>3</sub> (CT600) photocatalyst. Interfacial junctions between **a** CoTiO<sub>3</sub>-rutile-anatase phase and **b** CoTiO<sub>3</sub>-anatase-rutile phase of TiO<sub>2</sub>



the semi-circular diameter of CT600 is lower than that of T400 suggesting a lower charge carrier transfer resistance of CT600, which is in agreement with their photocurrent response results.

### 3.9 Photocatalytic mechanism and its schematic representation

The proposed photocatalytic mechanism of Co-TiO<sub>2</sub>/CoTiO<sub>3</sub> (CT600) photocatalyst is shown in Fig. 11a, b. The photogenerated charge carrier transfer mechanism is demonstrated through interfacial junctions that are type I (straddling) heterojunction between TiO<sub>2</sub> and CoTiO<sub>3</sub> and type II (staggered) homojunction of the anatase–rutile phase. Bandgap reduction in the host TiO<sub>2</sub> semiconductor after Co doping resulted due to the formation of impurity extremity at the uppermost part of the valence band (VB). The two possible ways of heterojunctions viz (a) CoTiO<sub>3</sub> with rutile-anatase and (b) CoTiO<sub>3</sub> with anatase–rutile sites of TiO<sub>2</sub> are demonstrated in Fig. 11a, b.

In the first case, the photoexcited electrons in the rutile phase readily migrates toward the energetically lower position conduction band (CB) of the anatase and CoTiO<sub>3</sub>. Likewise, the holes move from the VB of anatase to rutile and subsequently transfer to the VB of CoTiO<sub>3</sub>. In the latter case, the photogenerated electrons migrate from the rutile phase toward the CB of the anatase phase and eventually to CoTiO<sub>3</sub>. Correspondingly, the holes generated in the VB of the anatase phase travel toward the VB of CoTiO<sub>3</sub> and the rutile phase. The localized electric field at the interface can accelerate the transfer of charge between the anatase–rutile homojunction and the TiO<sub>2</sub>/CoTiO<sub>3</sub> heterojunction, which can further minimize

the recombination of electron–hole pair and ensures the availability of charge carriers for photocatalytic reactions, this could be also beneficial for fuel cells [18, 61].

## 4 Conclusion

The interfacial junction between anatase–rutile TiO<sub>2</sub> homojunction and CoTiO<sub>3</sub> heterojunction was tailored by employing a facile and cost-effective approach. The bandgap of TiO<sub>2</sub> was reduced by Co<sup>2+</sup> ion substitution and also increased surface oxygen vacancies that enhanced the photocatalytic reaction. The CT600 photocatalyst exhibited 97% degradation of MB dye within 90 min, which was 42-fold superior to that of pristine TiO<sub>2</sub>. The enhanced photocatalytic reaction mechanism of the CT600 catalyst can be demonstrated considering the two major aspects: high absorption across the visible light range and swift separation of charge carrier via homo and heterojunction in the Co-TiO<sub>2</sub>/CoTiO<sub>3</sub>. The significance of this photocatalyst is that it can effectively drive MB degradation present in polluted water sources in an economical and eco-friendly way. We believe that this CT600 photocatalyst can also be applied to a wide range of organic water pollutants such as methyl orange and methylene violet. In addition, this photocatalyst has the potential for application in water splitting for hydrogen production and can be used as an electrode in fuel cells.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s43207-022-00284-z>.

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**Data availability** The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Declarations

**Conflict of interest** The authors confirmed that there are no relevant financial or non-financial interests to declare.

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