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Md. Minhajul Islam

Rajshahi University of Engineering & Technology

Hridoy Roy

Rajshahi University of Engineering & Technology

Kashfi Uddin

Chittagong University of Engineering and Technology (CUET)

Abdullah Al Mahmood

Rajshahi University of Engineering & Technology

Md. Bodiul Islam

Rajshahi University of Engineering & Technology

Md. Mukter Hossain

`mukter_phy@cuet.ac.bd`

Chittagong University of Engineering and Technology (CUET)

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Structural, Electronic, Optical and Photocatalytic Activity of Zn doped CaTiO₃ Compounds: A Combined Experimental and DFT Approach

Md. Minhajul Islam¹, Hridoy Roy¹, Kashfi Uddin², Abdullah Al Mahmood¹, M. Bodiul Islam^{1*}, Md. Mukter Hossain^{2,*}

¹ Nano Synthesis Laboratory, Department of Ceramic & Metallurgical Engineering, Rajshahi University of Engineering & Technology, Kazla, Rajshahi 6204, Bangladesh

²Department of Physics, Chittagong University of Engineering and Technology (CUET), Chattogram-4349, Bangladesh

*Corresponding author, e-mail: mukter_phy@cuet.ac.bd (Md. Mukter Hossain)
mbi@cme.ruet.ac.bd (Md. Bodiul Islam)

Abstract

Zinc-doped Zn_xCa_{1-x}TiO₃ with x values of 0, 0.03, and 0.06 were produced by a standard solid-state reaction technique utilizing a stoichiometric molar ratio for enhanced photocatalytic activity. The structural and electronic properties were investigated using density functional theory (DFT) to validate the experimental results. X-ray diffraction was used to study how different calcination temperatures and dopants' concentrations affected the solid-state chemical synthesis and the structure and crystal size of CaTiO₃ (CTO). All of the diffraction peaks under study were associated with the orthorhombic structure. After doping CTO with 6% Zn, the SEM shows a rougher surface with narrower grain boundaries, while the FTIR spectrum indicates bond stretching and vibration. The photocatalytic degradation of methylene blue on both pure and Zn-doped CTO particles under UV–visible light has been scrutinized. The findings indicate that Zn doping substantially improved the visible-light absorption capacity of CaTiO₃ by reducing the bandgap from approximately 3.52 to 3.07 eV. The observed band gap reduction was further validated through DFT calculations. In addition, the lattice parameters of both pristine and doped structures were systematically evaluated. The theoretically obtained values showed good agreement with the experimental data. Subsequently, an augmented photocatalytic activity of 95.05% was achieved through Zn doping of CTO.

Keywords: Perovskite; Solid state reaction; DFT; UV-visible light; Photocatalytic activity.

1. Introduction

In recent decades, significant attention has been devoted to the photocatalytic degradation and complete mineralization of hazardous organic pollutants in water, soil, and air using semiconductor-based materials [1]. This focus is driven by rapid industrialization, which has intensified global energy demand and environmental remediation challenges [2]. Semiconductor photocatalysis is a promising and cost-effective approach for both solar energy conversion to meet increasing global energy demand and environmental purification. Since the initial report of electrochemical photolysis of water at a TiO_2 electrode, semiconductor-based photocatalysis has been widely used to degrade organic contaminants in air or water and to split water [3]. In this context, researchers are fascinated by titanium dioxide (TiO_2) for killing germs, getting rid of odours, and cleaning air and water since it is biologically and chemically inert, non-toxic, and stable over time. Most of these uses, however, are ineffective due to their low quantum efficiency [4]. TiO_2 , ZnO , CdS , WO_3 , BiVO_4 , etc., are among the most studied photocatalysts [5] for degrading organic pollutants in water or gas, but their large band gaps and stability issues have limited their usefulness in the visible-light range [6,7]. As it has a relatively wide band gap, TiO_2 only works in the ultraviolet range and lets through about 5% of the sun's light that reaches Earth. As a result, considerable effort has gone into improving its ability to absorb visible light (420 to 750 nm), which accounts for 43% of the sun's light reaching Earth [8]. The study of the luminescence behavior of the perovskite structure ATiO_3 ($\text{A}=\text{Pb}$, Ca , Sr , and Ba) has recently attracted considerable attention due to its distinct optical, thermal, electrical, and mechanical properties, which can be used to create promising phosphor materials [9]. Furthermore, perovskite-type oxides have attracted significant attention in recent decades due to their structural versatility and tunable physicochemical properties, which make them promising candidates for a wide range of solar energy and environmental applications. Among these materials, calcium titanate (CaTiO_3) has emerged as an important semiconductor photocatalyst owing to its chemical stability, non-toxicity, and relatively low cost [5]. Researchers are quite interested in calcium titanate because of its intriguing ferroelectricity, piezoelectricity, elasticity, and photocatalytic activity characteristics [10]. Its orthorhombic perovskite structure provides a robust framework that accommodates various modifications, enabling tailoring of its electronic structure and surface properties to enhance photocatalytic performance. However, the practical application of CaTiO_3 is often limited by its wide band gap, which primarily restricts its photo-response to the ultraviolet region, and by the rapid recombination of photogenerated electron-hole pairs. These limitations significantly reduce its

quantum efficiency under solar irradiation. To overcome these challenges, various strategies have been developed, including elemental doping, surface modification, heterojunction construction, and nano-structuring. Such approaches aim to extend light absorption into the visible region, improve charge separation efficiency, and increase the availability of active sites [11]. When exposed to solar radiation with photon energy ($h\nu$) that is equal to or greater than the bandgap energy (E_g), it is necessary to make non-noble metal-based photocatalysts that work well. In particular, elemental doping has shown considerable promise in enhancing photocatalytic activity through synergistic effects. Basic mechanism of photocatalytic activity of pure and metal (like Zn)-doped CaTiO_3 is shown in Fig. 1.

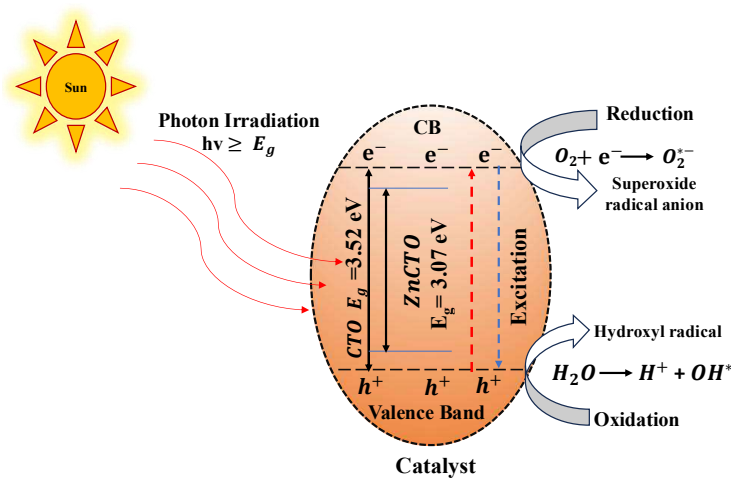


Fig. 1: Basic mechanism of photocatalysis with CTO and Zn-doped CTO.

The catalytic activity of a semiconductor photocatalyst depends on several parameters, such as its crystallinity, defects, microstructures, and others. Controlling these parameters has been an effective way to modify the photocatalytic activity of a specific semiconductor material. The current research examines how effectively pure and non-noble metal-doped CaTiO_3 particles act as photocatalysts, and how suitable the solid-state reaction route is compared with other ways of making CTO reported in the literature [12–17].

In this work, $\text{Zn}_x\text{Ca}_{1-x}\text{TiO}_3$ powder is synthesized via the solid-state reaction technique with x values of 0, 0.03, and 0.06. The effects of process parameters and composition on the photocatalytic activity of $\text{Zn}_x\text{Ca}_{1-x}\text{TiO}_3$ are investigated to contribute to the development of efficient and sustainable photocatalytic materials. To validate the experimental results, the structural and electronic properties are also investigated using density functional theory (DFT).

This research article is the first combined experimental and DFT study of the photocatalytic activity of Zn-doped CTO in breaking down the methylene blue (MB) dye.

2. Materials and methods

To synthesize pure and doped CTO, a solid-state reaction method was adopted. The precursor materials were all chemical-grade reagents bought from LOBA CHEMIE PVT. LTD., India. The photocatalytic activity of both pure and Zn-doped CTO in the UV-visible light range was investigated.

2.1 Preparation of pure CaTiO_3

A stoichiometric amount of the collected CaCO_3 and TiO_2 was mixed with ethanol, then milled to ensure uniformity. To produce 25 gm of CaTiO_3 , 18.58 gm of CaTiO_3 and 14.98 gm of TiO_2 were used. The milling took 24 hours and used Zirconia balls as the milling media. The solution was then dried to a powder, and the resulting powders were pressed into pellets using a hydraulic press at 5 tons. The tablet samples were then put into a crucible. The sintering was placed in an electric furnace (Nabertherm GMBH, UK) at 1200 °C for 4 hours. Fig. 2 shows the sintering cycle for pure CaTiO_3 . After air cooling, the tablet shape was ground into powder.

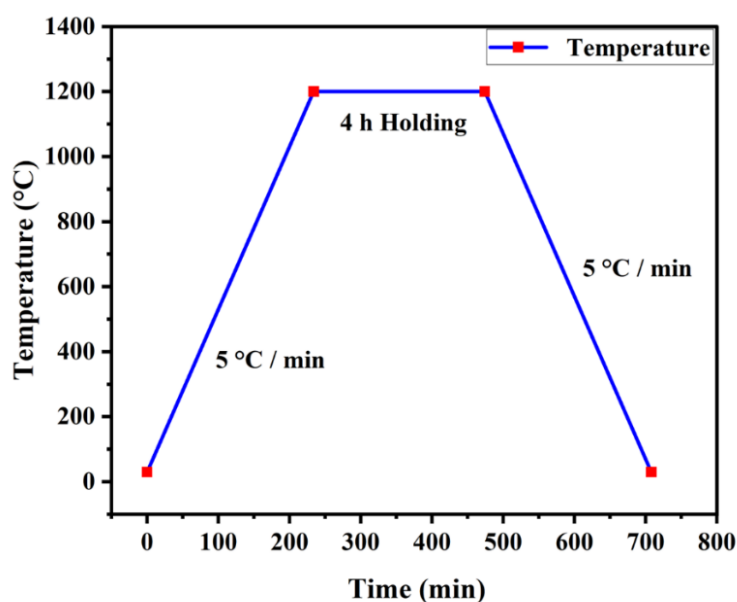


Fig. 1: Sintering cycle of the CaTiO_3 sample.

2.2 Preparation of Zn-doped CaTiO_3

To make Zn-doped CaTiO_3 , an ethanol solution of zinc acetate was added to an ethanol suspension of CaTiO_3 . For four hours, the precursor solution was stirred to facilitate ethanol evaporation. After that, the powders were heated to 900°C for two hours. Fig. 3 represents the calcination cycle for Zn-doped CaTiO_3 . Before the photocatalytic property tests and other characterizations, the solids that were made were ground into very fine powders.

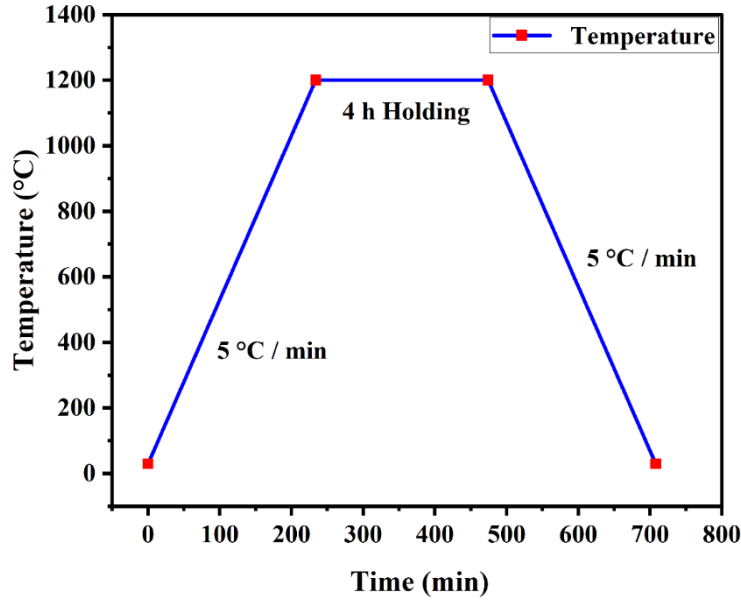


Fig. 2: Sintering cycle of Zn-doped CaTiO_3 sample.

2.3 Computational Study

Density Functional Theory (DFT) calculations are carried out using the Vienna Ab initio Simulation Package (VASP) [18,19]. Pristine CaTiO_3 is simulated using its unit cell, whereas $8 \times 1 \times 1$ and $1 \times 8 \times 1$ supercells are constructed to represent 3.125% and 6.25% Zn-doped compounds, respectively. The interaction between electrons and ions is described using the Projector-Augmented-Wave method [20,21] with a plane-wave cutoff energy of 500 eV. Exchange-correlation effects are treated within the generalized gradient approximation (GGA) [22] using the Perdew-Burke-Ernzerhof for solids (PBEsol) [23] functional with Hubbard correction (GGA+U) [24]. Monkhorst-Pack [25] k-point meshes of $5 \times 3 \times 5$, $1 \times 3 \times 5$, and $4 \times 1 \times 5$ are applied for pristine CaTiO_3 , $\text{Ca}_{0.97}\text{Zn}_{0.03}\text{TiO}_3$, and $\text{Ca}_{0.94}\text{Zn}_{0.06}\text{TiO}_3$, respectively. All the studied structures are fully relaxed until the forces converged to 1×10^{-2} eV/Å and the electronic energy reaches a convergence criterion of 1×10^{-4} eV. A k-point spacing of

approximately $0.04 \text{ \AA}^{-1}$ is maintained to ensure reliable geometric optimization and accurate electronic property calculations.

To better describe the localized d-electrons, the Hubbard U correction is introduced using the Dudarev approach [26], which accounts for the on-site Coulomb interaction of the *Ti 3d* and *Zn 3d* states. The GGA-PBEsol functional is employed as the exchange-correlation approximation to optimize the lattice parameters and atomic positions. The experimental band gap is reproduced by carefully tuning the effective Hubbard U values using a linear-response approach [24], yielding values between 5.24 and 5.91 eV for Ti and 5.47 and 5.80 eV for Zn. In addition to these, the crystal structures are generated and visualized using the VESTA software [27].

3 Results and Discussion

3.1 Characterization of synthesized samples

3.1.1 Structure and surface morphology

X-ray diffraction analysis (LabX XRD-6100, Shimadzu, Japan) was performed to examine the structure of the particles. We used CuK ($\lambda = 0.154056 \text{ nm}$) radiation and scanned the range of $2\theta = 20\text{--}80^\circ$ at a speed of $2^\circ/\text{min}$ and a step of 0.02° . Scanning electron microscopy (JCM-6000 Plus, JEOL, Japan) helped us understand the surface morphology of the samples we generated.

3.1.2 FT-IR and optical properties

FT-IR spectroscopy was performed on both pure CaTiO_3 and Zn-doped CaTiO_3 using a Perkin Elmer Frontier FT-IR spectrometer. To testify to the optical properties of the produced materials, a UV–VIS–NIR Spectrophotometer (UV-2600, Shimadzu, Japan) is employed. To determine a compound's optical bandgap while accounting for absorbance, using the Tauc plot of $(\text{band energy, } h\nu)^n$ versus h [28]. Here, $h\nu$ stands for incident photon energy, A for constant, and E_g for optical bandgap. The energy gap for indirect ($n = 1/2$) electronic transitions might be measured by extrapolating from the linear parts of Tauc's plots, i.e., $(h\nu)^n$ versus $(E = h\nu)$ to zero absorption [29]. The original Tauc plot method was developed primarily for amorphous bulk semiconductors and non-direct inter-band transitions. For direct interband transitions, the original Tauc plot approach was later created. This method's drawback, though, is that the Tauc plot was developed without accounting for the different physical processes that could occur. When a single interband transition forms the absorption edge, this technique can be used [30].

3.1.3 Photocatalytic sample preparation

The photocatalytic properties have been studied by examining how the methylene blue (MB) dye breaks down under UV light. A UV–VIS-NIR Spectrophotometer (UV-2600, Shimadzu, Japan) was used to test how well MB samples absorbed light. Firstly, a 0.2 g sample of a photocatalyst (CTO) was mixed with 100 mL of an aqueous methylene blue solution containing 10 mg/L of the chemical. Before irradiation, the aqueous solution was magnetically stirred in the dark for 15 minutes to reach equilibrium between MB adsorption and desorption on the sample surface. The source of the radiation was a 664 nm UV light. At this stage, 5.0 mL samples of the suspension were centrifuged for 10 minutes at 4000 rpm and then taken to a dark environment. Next, the solution was put to the test. Finally, the decrease in MB's absorption intensity has been used to measure the photocatalytic degradation of MB. The following equation was used for calculating the photocatalytic degradation:

Degradation percentage [31],

$$D (\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (2)$$

Here,

A_0 = Absorbance at time 0 minutes, A_t = Absorbance at time t minutes (t = 0, 40, 80 and 120 minutes respectively).

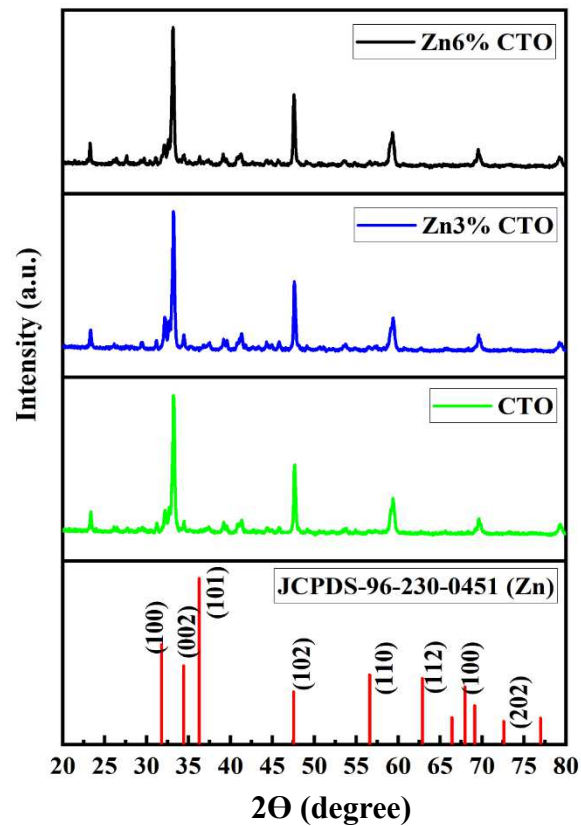


Fig. 3 : XRD image of CaTiO₃ and Zn doped CaTiO₃ with JCPDS card of Zn.

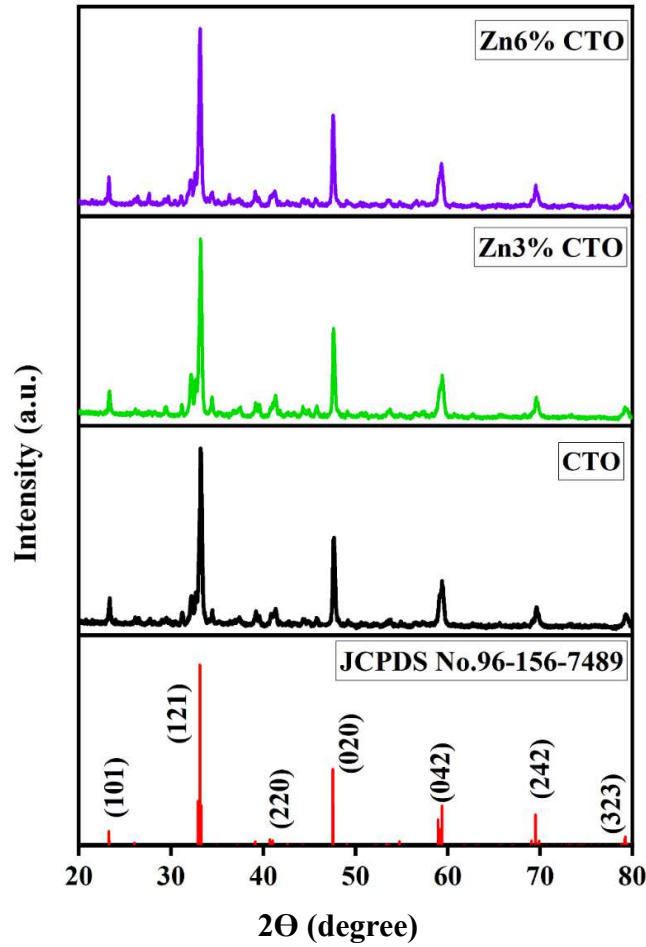


Fig. 4 : XRD image of pure and Zn-doped CaTiO_3 .

3.2 Analysis of structure by X-ray diffraction and DFT

XRD was used to examine the crystalline forms of pure CaTiO_3 (CTO) and CaTiO_3 doped with Zn. **Fig. 5** shows that all five XRD patterns of CTO exhibited diffraction peaks at $2\theta = 23.18^\circ$ (101), 33.09° (121), 47.49° (020), 59.32° (042), and 69.50° (242). The JCPDS database (No. 961567489) indicates that these peaks correspond to CaTiO_3 , which has an orthorhombic perovskite structure. The strongest peak is at $2\theta \sim 33.096^\circ$, corresponding to the (121) plane. The Ca^{2+} ion in orthorhombic CaTiO_3 is connected to eight oxygen atoms, which makes a deformed dodecahedron. The Ti^{4+} ion is coordinated by six O^{2-} ions in an octahedral arrangement [32]. The JCPDS database (No. 962300451) in **Fig. 4** indicates that these peaks indicate the presence of Zn. There were no impurities or phases associated with Zinc in these XRD patterns. This research uncovers that adding Zn makes CaTiO_3 crystals more stable [33]. Fig. 6 shows that the peak shifted to a lower 2θ value. This occurred because introducing Zn^{2+}

into the Ca^{2+} site caused the peak to shift toward a lower diffraction angle. This is because Zn^{2+} has a smaller ionic radius than Ca^{2+} . Scherrer's formula was used to figure out the average size D of the films' crystallites [28].

$$D = \frac{(0.94 \lambda)}{\beta \cos \theta} \quad (1)$$

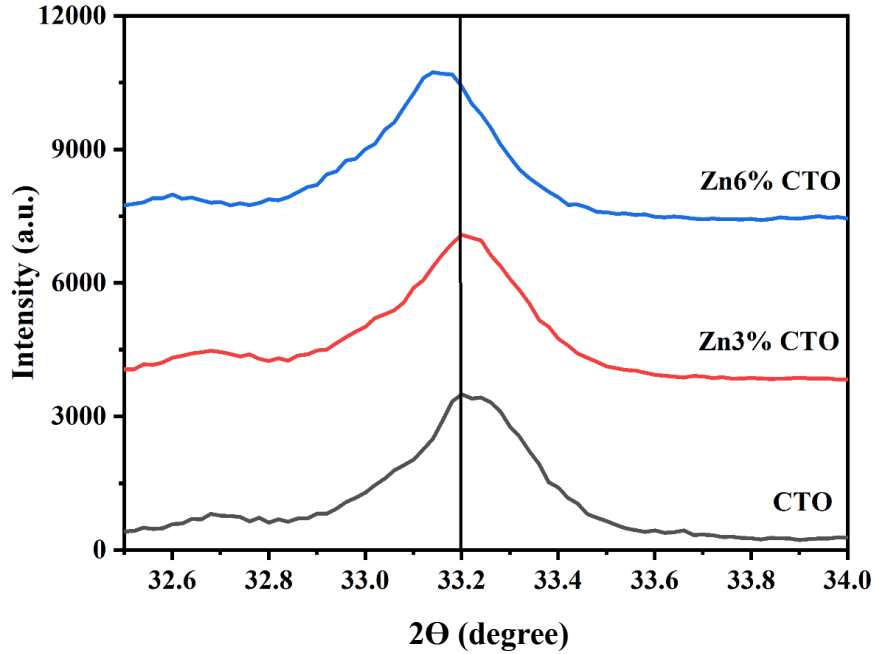


Fig. 5 : XRD patterns revealing a shift in the peak of the (121) plane of pure and Zn-doped CaTiO_3 .

The highest diffraction peak of Eu-doped CaTiO_3 was at $2\theta=33.183$, which is the same as the crystalline plane with Miller indices (121). The Zn^{2+} ions take the place of the Ca^{2+} ions in the host CaTiO_3 because the ionic radius of Zn^{2+} (0.74) is close to that of Ca^{2+} (0.99). So, the XRD examination shows that the Zn-doped CaTiO_3 has formed.

Calcium titanate crystallizes in an orthorhombic perovskite structure belonging to the Pnma space group. In this arrangement, Ca^{2+} ions are coordinated by eight O^{2-} atoms, while Ti^{4+} ions are surrounded by six O^{2-} atoms, forming corner-sharing TiO_6 octahedra. The conventional unit cell contains 20 atoms, equivalent to four formula units. The Ti atoms occupy the 4b Wyckoff position (0, 1/2, 1/2), Ca atoms are located at the 4c position (0.509, 0.542, 3/4), and O atoms are distributed over the 4c (0.076, 0.481, 3/4) and 8d (0.790, 0.789, 0.959) sites. The optimized unit cell of pristine CaTiO_3 and the supercells constructed for Zn-doped structures are illustrated in Fig. 7, while the influence of Zn incorporation on the lattice parameters is summarized in Table 1. The calculated lattice constants show good agreement with the experimental values, with deviations of less than 5 %, confirming the reliability of the numerical work.

Table 1: Numerically calculated lattice parameters and the band gap of the studied compounds and their deviation percentage relative to the experimental data.

<i>Compound</i>	<i>Lattice Parameters(Å)</i>						<i>Band gap(eV)</i>		<i>Ref</i>
	<i>a</i>	<i>%dev</i>	<i>b</i>	<i>%dev</i>	<i>c</i>	<i>%dev</i>	<i>gap</i>	<i>%dev</i>	
<i>Pristine CaTiO₃</i>	5.38	0.56	7.64	0.62	5.44	1.29	3.52	4.55	Exp.
	5.41		7.69		5.51		3.36		Theo.
	5.40		7.64		5.42		3.29		[11]
<i>3% Zn doped</i>	5.39	0.19	7.63	0.79	5.43	1.66	3.29	4.56	Exp.
<i>3.125% Zn doped</i>	5.40		7.69		5.52		3.14		Theo.
<i>6% Zn doped</i>	5.40	1.11	7.64	0.65	5.42	4.24	3.07	3.26	Exp.
<i>6.25% Zn doped</i>	5.34		7.59		5.65		2.97		Theo.

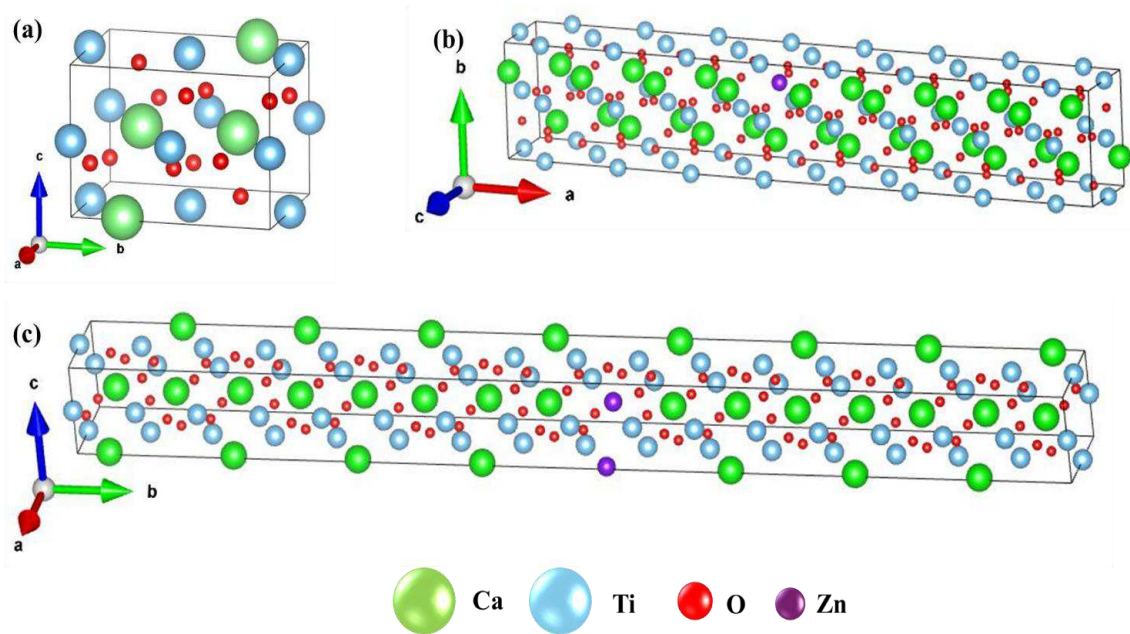


Fig. 6: The unit cell and supercell structures of the (a) pristine CaTiO₃, (b) 3.125% Zn doped, and (c) 6.25% Zn doped structures.

3.3 Morphological analysis

3.3.1 Analysis by SEM

Fig. 8 shows the surface shapes of pure and Zn-doped CaTiO_3 samples. Morphological properties were observed using scanning electron microscopy (SEM), and Table 2 presents the grain sizes consistent with them. SEM examination showed particle agglomeration and that grain size changed noticeably with Zn doping [34]. **Fig. 8** shows that the pure CaTiO_3 particles are nanorod-like. When Zn is added, this shape changes to a more granular one. This change in shape indicates that the dopant affects the processes of nucleation and growth, causing particles to stick together and become denser. The observed agglomeration behavior can be attributed to a reduction in surface energy concomitant with an increase in particle size and a commensurate decrease in specific surface area. This effect is consistent with the fundamental concept of particle agglomeration, which states that larger particles exhibit reduced surface free energy, hence enhancing their propensity to agglomerate. Moreover, the SEM micrographs demonstrate that the 6% Zn-doped CaTiO_3 sample has a surface that is rougher and more open than the undoped or less-doped samples. The higher surface roughness and porosity create more active surface sites, thereby favoring photocatalytic reactions. The particle size distribution histogram supports this result by showing that the 6% Zn-doped sample has a wider and more varied size range.

Table 2. FWHM, Crystallite size, and grain boundary of the fabricated sample.

Sample Name	Crystallite size (nm)	FWHM	Grain boundary (nm)
Pure CTO	24.05	0.4173	40.48
3% Zn doped CTO	24.24	0.5447	34.26
6% Zn doped CTO	26.90	0.3758	28.79

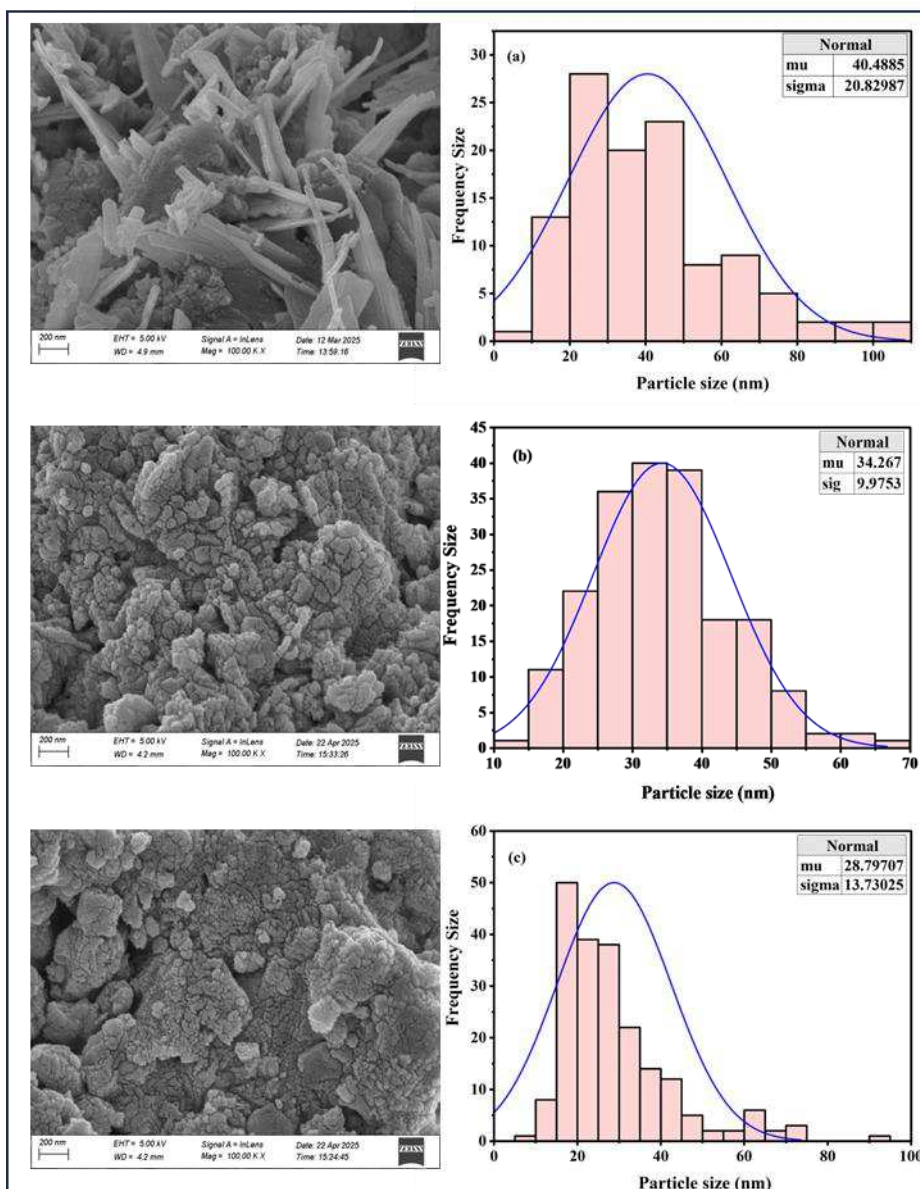


Fig. 7 : SEM images and their particle size distribution of the (a) pristine CaTiO_3 , (b) 3.00 % Zn doped, and (c) 6.00 % Zn doped structures.

3.3.2 EDX

The SEM micrographs of $\text{Zn}_x\text{Ca}_{1-x}\text{TiO}_3$ ($x = 0.03$ & 0.06) samples exhibit a highly porous surface morphology. The concentration of Zn doping has a significant impact on grain size in the samples. The average grain size decreases as the amount of Zn increases. So, adding Zn hinders grain expansion during synthesis and encourages the production of smaller particles with larger surface areas. EDX images confirmed the presence of constitutional elements and dopants in **Fig. 9**.

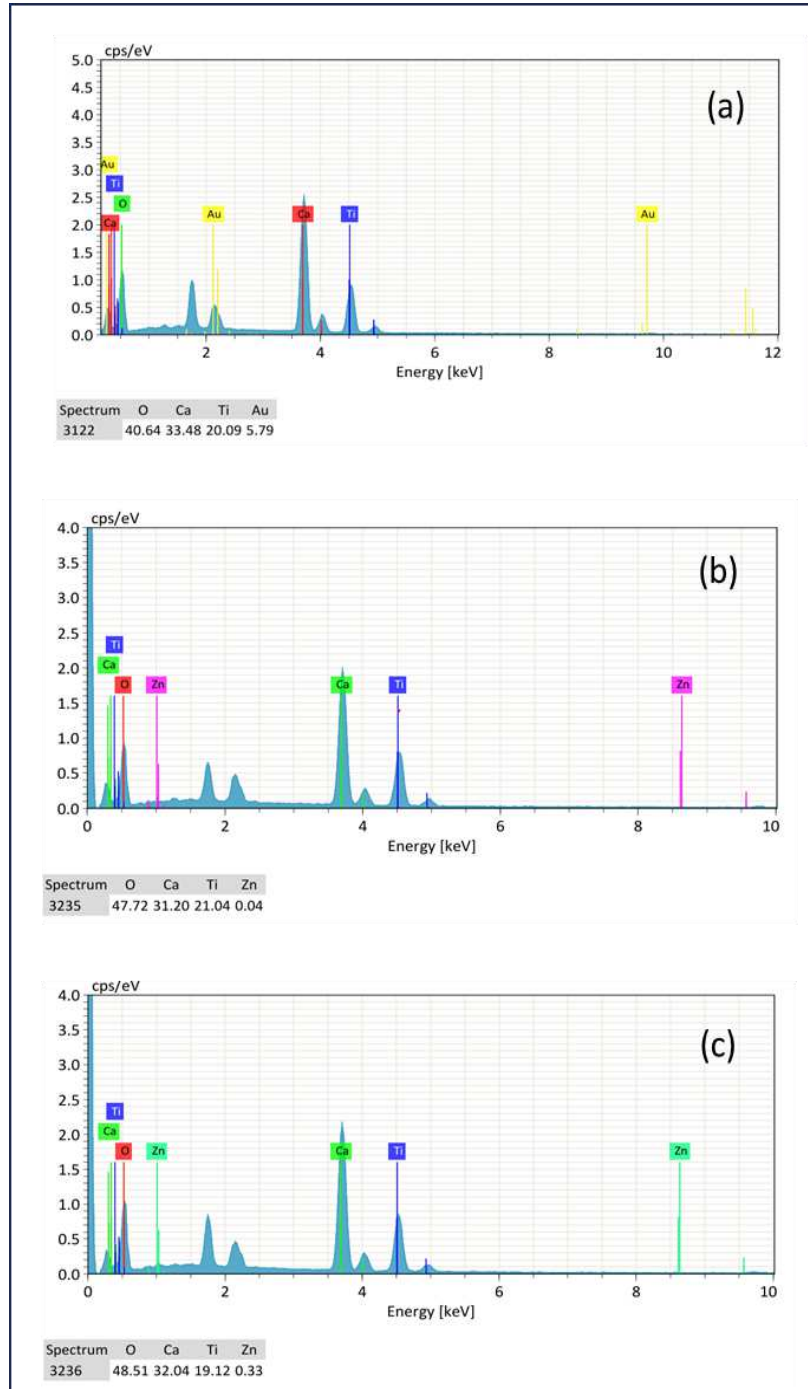


Fig. 8 : EDX image of (a) pristine (CaTiO_3), (b) Zn 3% CaTiO_3 , (c) Zn 6% CaTiO_3 .

3.4 FT-IR analysis

The BaTiO₃ doped with potassium has an absorption peak at 544 cm⁻¹, because the lattice parameter changed, when K⁺ replaces Ba²⁺, the cell parameter gets lower because K⁺ has a smaller radius than Ba²⁺, then the space between Ti and O gets smaller and the Ti–O connection gets stronger. After that, the BaTiO₃ material doped with K shows a higher absorption peak wavenumber. When a K⁺ replaces a Ba²⁺, charge is generated. When a Li⁺ (or Na⁺) replaces a Ti⁴⁺, it makes three negative electric charges. The number of O⁻ vacancies in the latter is three times that in the former to maintain electric charge balance. Because of this, it is easier to bend or break Ti–O octahedra. The periodic structure of the crystal determines the energy of lattice vibration, which makes it less [35]. The absorption peak at about 540 cm⁻¹ is due to the vibration of the O–M (M=ion at B-site) link, because the oxygen octahedra in these two systems are highly similar, even though some ions are different. The vibration of the Ti–O bond, on the other hand, is complicated. When the amount of Ca in BaTiO₃ increases, the absorption peak wavenumber shifts to a higher value as the cell size decreases, thereby increasing the binding energy [36]. The wavenumber of the Ti–O bond absorption peak increases as the amount of Ca increases, even though the amount of Ti remains the same. The absorption peak in (Ba_{0.95}Ca_{0.05})TiO₃ is around 525 cm⁻¹, and the absorption peak in (Ba_{0.80}Ca_{0.20})TiO₃ is around 550 cm⁻¹. It is because the cell size has gotten smaller. Replacing Ca with Ti–O shortens the bond length. Then the way Ti and O interact gets stronger [37,38]. **Fig. 10** reveals the FTIR spectra of both pure and Zn-doped CaTiO₃ (CTO) samples. The characteristic absorption bands seen between 400 and 4000 cm⁻¹ are due to the basic vibrational patterns associated with metal–oxygen bonds and functional groups on the surface. The undoped CTO sample has a broad absorption below 600 cm⁻¹. This is largely because the Ti–O linkages in the TiO₆ octahedra are stretching. This shows that the perovskite phase has developed. Adding Zn makes the spectrum look very different. The Zn 3 % CTO and Zn 6 % CTO samples exhibit distinct absorption peaks: one at approximately 584 cm⁻¹ and the other at approximately 465 cm⁻¹. These peaks correspond to Ti–O and Zn–O stretching vibrations, respectively. The Zn–O band shows up, which means that Zn²⁺ ions have taken the position of Ca²⁺ ions in the CTO lattice. Because the ionic radii of Zn²⁺ and Ca²⁺ do not match, this form of substitution generates local lattice distortions. This strengthens the metal–oxygen bonds and raises the absorption peaks slightly in wavenumber.

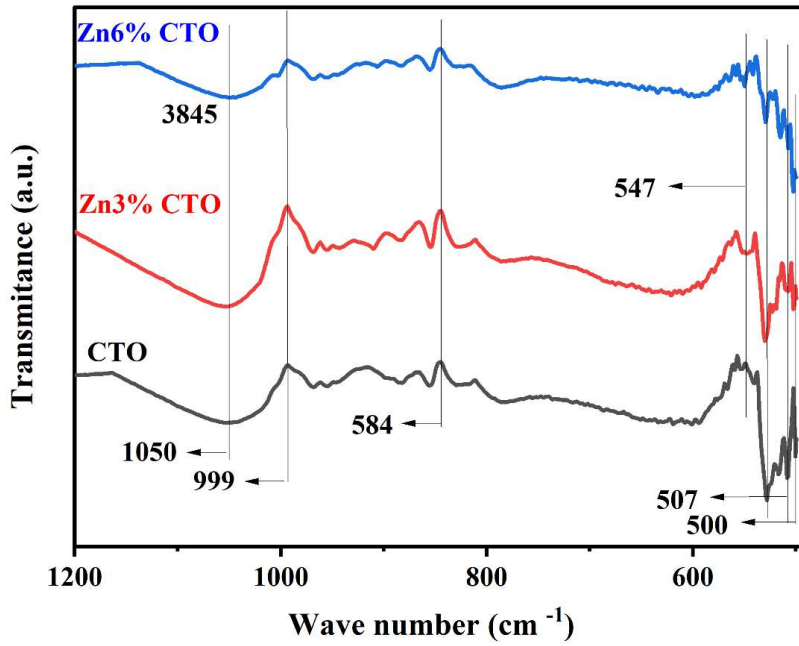


Fig. 9: FTIR image of CaTiO_3 and Zn-doped CaTiO_3 .

In the pure CTO sample, there is a weak absorption band about 3845 cm^{-1} . The stretching vibration of surface hydroxyl ($-\text{OH}$) groups and adsorbed water molecules causes this band. The band gets smaller in the Zn-doped samples, suggesting that doping removes surface hydroxyl species and adsorbed moisture. The reduction in hydroxyl groups signifies enhanced crystallinity and a diminished presence of surface imperfections on the particles.

The presence of bands at 568 cm^{-1} and 465 cm^{-1} further substantiates the formation of Zn–O bonds, consistent with previously reported values for Zn-doped perovskite oxides [37]. These results confirm that incorporating Zn modifies the structural and surface characteristics of CaTiO_3 , leading to improved metal–oxygen interactions and enhanced structural stability. The absorption bands at 584 cm^{-1} and 465 cm^{-1} are due to stretching vibrations of Ti–O and Zn–O, which show that Zn has been added to the perovskite lattice. The weak band at about 3845 cm^{-1} , attributed to $-\text{OH}$ groups, is weaker when Zn is added. This means that surface hydroxyl species are being removed.

3.5 Optical band gap

The optical band gap energies that are pure CTO, Zn 3 %-doped CTO, and Zn 6 %-doped CTO are 3.52 eV, 3.29 eV, and 3.07 eV, respectively, as substantiated in **Fig. 11**. The band gap energy gradually decreases as the amount of Zn increases. Adding Zn changes the electronic structure of CaTiO_3 , creating localized energy states near the conduction band. When the band gap is smaller, the material can absorb more visible light and excite charge carriers. The Zn 6%-doped CTO sample has the smallest band gap (3.07 eV), making it the most likely to be used in optoelectronic devices and for photocatalysis under visible light.

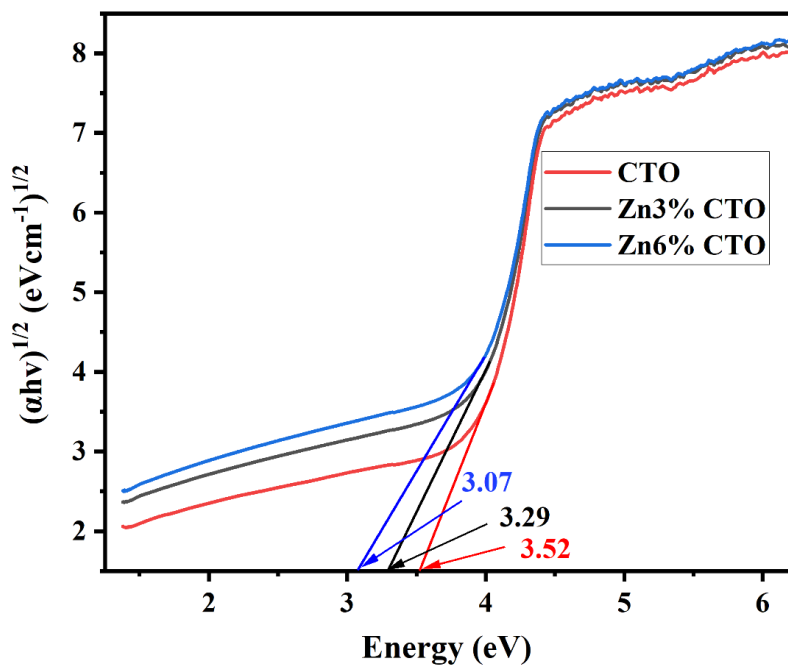


Fig. 10 : Energy Bandgap of (a) CaTiO_3 , (b) Zn 3 % CaTiO_3 , (c) Zn 6 % CaTiO_3 .

The calculated band gaps show good agreement with the experimental values, as summarized in Table 1. Fig. 12 presents the electronic band structures of pristine and Zn-doped Calcium titanate, calculated along high-symmetry points in the Brillouin zone. The valence and conduction bands are separated by the Fermi level (E_F), which serves as the reference energy. The band gap corresponds to the energy difference between the top of the valence band and the bottom of the conduction band and determines the electronic nature of the material. For pristine CaTiO_3 , the band structure confirms its semiconducting character with a direct band gap at the Γ point. When Zn substitutes at the Ca site, noticeable changes in the electronic structure arise from the presence of fully occupied $\text{Zn-}3d$ states.

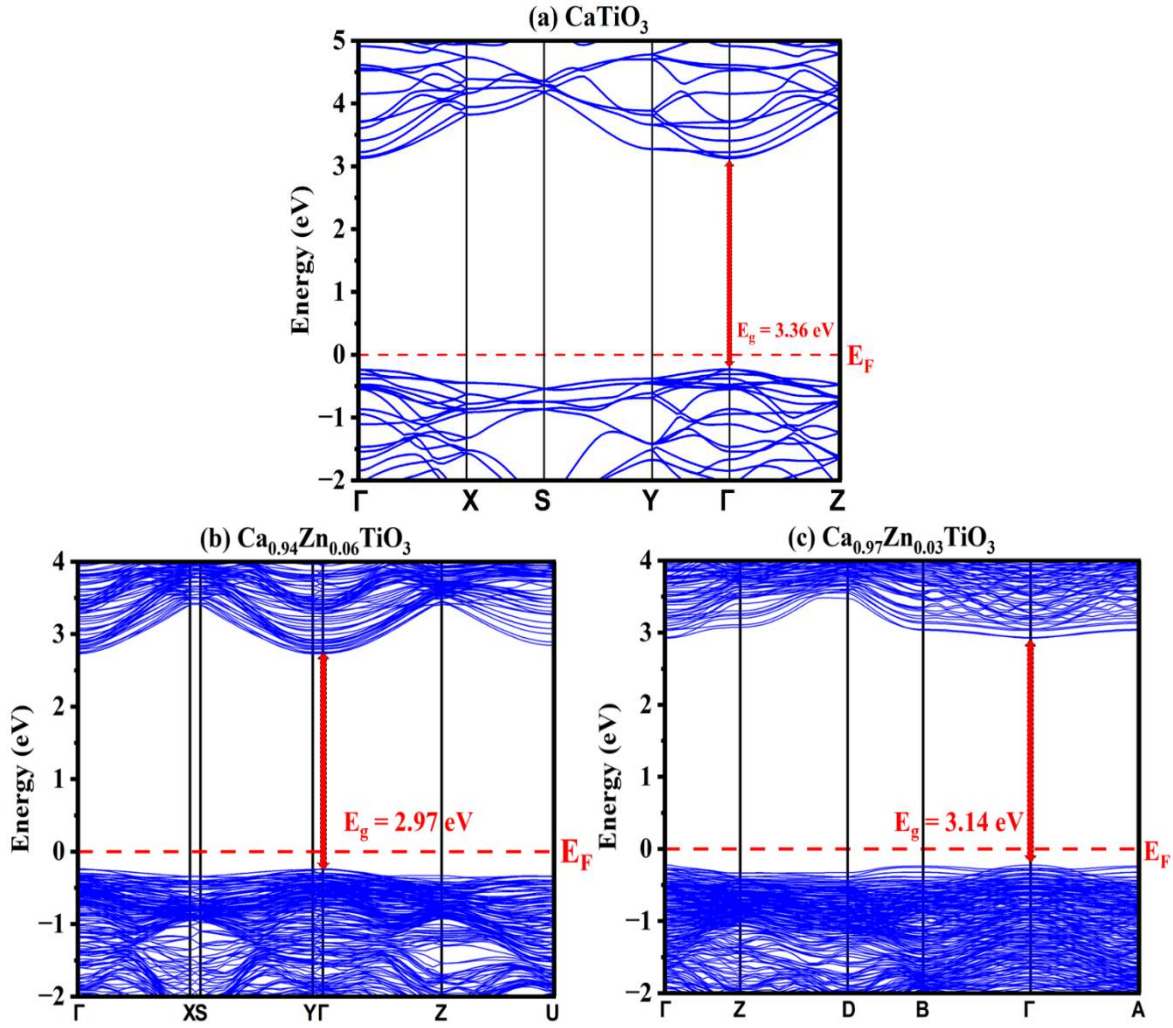


Fig. 11: Calculated band structure of the (a) pristine CaTiO_3 , (b) 6.25% Zn doped and (c) 3.125% Zn doped structures.

3.6 Absorbance

Fig. 13 presents the UV–Vis absorption spectra of pure CTO and Zn-doped CTO (Zn 3 %–CTO and Zn 6 %–CTO). The UV absorption (200–300 nm) is mostly due to intrinsic electronic transitions within the CTO lattice. There is a clear absorption edge near 300 nm, indicating the material's band gap. Adding Zn to CTO escalates its ability to absorb light across the entire spectrum. Zn 6%–CTO has the highest absorption, indicating that adding Zn enhances CTO's light-absorbing ability. The electronic structure may have been amended, and defect or impurity levels may have been introduced in the band gap, which could explain this improvement. Also, samples containing Zn absorb more light in the visible range (400–900 nm), indicating they can collect more light and could be used in photocatalytic and optoelectronic devices.

3.7 Photocatalytic degradation

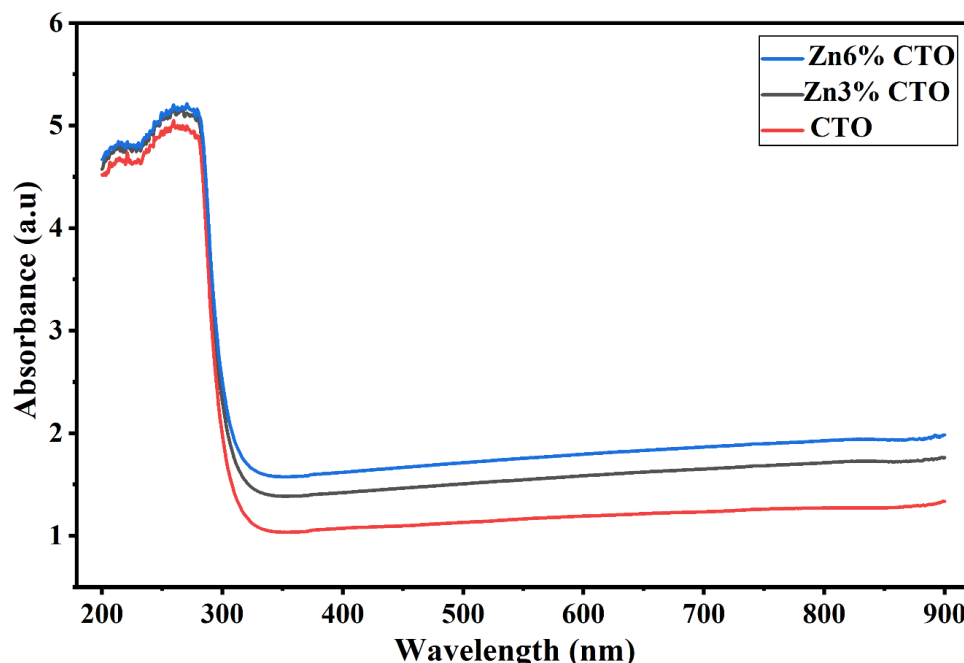


Fig. 12 : Absorbance of (a) CaTiO_3 , (b) Zn 3 % CaTiO_3 , (c) Zn 6 % CaTiO_3 .

Methylene blue (MB) dye was used as a model organic contaminant to test the photocatalytic efficacy of the produced CaTiO_3 (CTO) and Zn-doped CaTiO_3 samples under UV-visible light. Intrinsic defects, oxygen vacancies, surface states, and structural deviations that serve as charge-trapping sites are the main factors affecting the photocatalytic degradation mechanism. **Fig. 1** shows the basic mechanism of photocatalytic activity. Oxygen vacancies and surface defects can trap photoexcited electrons that move from the valence band (VB) to the conduction band (CB). Because this configuration is kinetically substantial within the CB region [37].

Fig. 14 illustrates that all the samples have an absorption peak for MB at 664 nm. This peak diminished over time, which denotes that the dye was gradually disintegrating. The fading hue of the MB solution supports this finding. After 120 minutes of light, the degradation curves of the Zn-doped CTO sample were almost plateaued and completely discolored **Fig. 17**. The diminution in absorbance with time, as shown in Table 3 indicates that MB was rapidly degraded via photocatalysis.

The absorbance spectra in **Fig. 14** and Table 4 indicate that the pure CTO catalyst decomposed 82.18 % of the material, whereas the Zn 3 %- and Zn 6 %-doped CTO samples decomposed 92.48 % and 95.07 %, respectively, after 120 minutes of irradiation. **Fig. 15**

reveals how the concentration ratio (C_t/C_0) changes over time for each catalyst. This fits the Langmuir–Hinshelwood model, which mentions that the reaction is pseudo-first order [39]. **Fig. 16** presents linear plots of $\ln(C_t/C_0)$ versus irradiation time, yielding rate constants (k) of 0.01406 min^{-1} , 0.02025 min^{-1} , and 0.02542 min^{-1} for CTO, Zn 3 % CTO, and Zn 6 % CTO, respectively.

Table 3. At 664 nm wavelength, multiple peak absorbance for each interval of pure and Zn-doped CaTiO_3 .

Time (min)									
Elements	00	15	30	45	60	75	90	105	120
CaTiO_3	1.937	1.640	0.84667	1.1811	0.16644	0.813	0.619	0.469	0.345
Zn 3 % CaTiO_3	1.890	1.539	0.81128	1.23262	0.20914	0.607	0.454	0.253	0.142
Zn 6 % CaTiO_3	1.827	1.688	1.08235	0.92392	0.07913	0.540	0.286	0.171	0.090

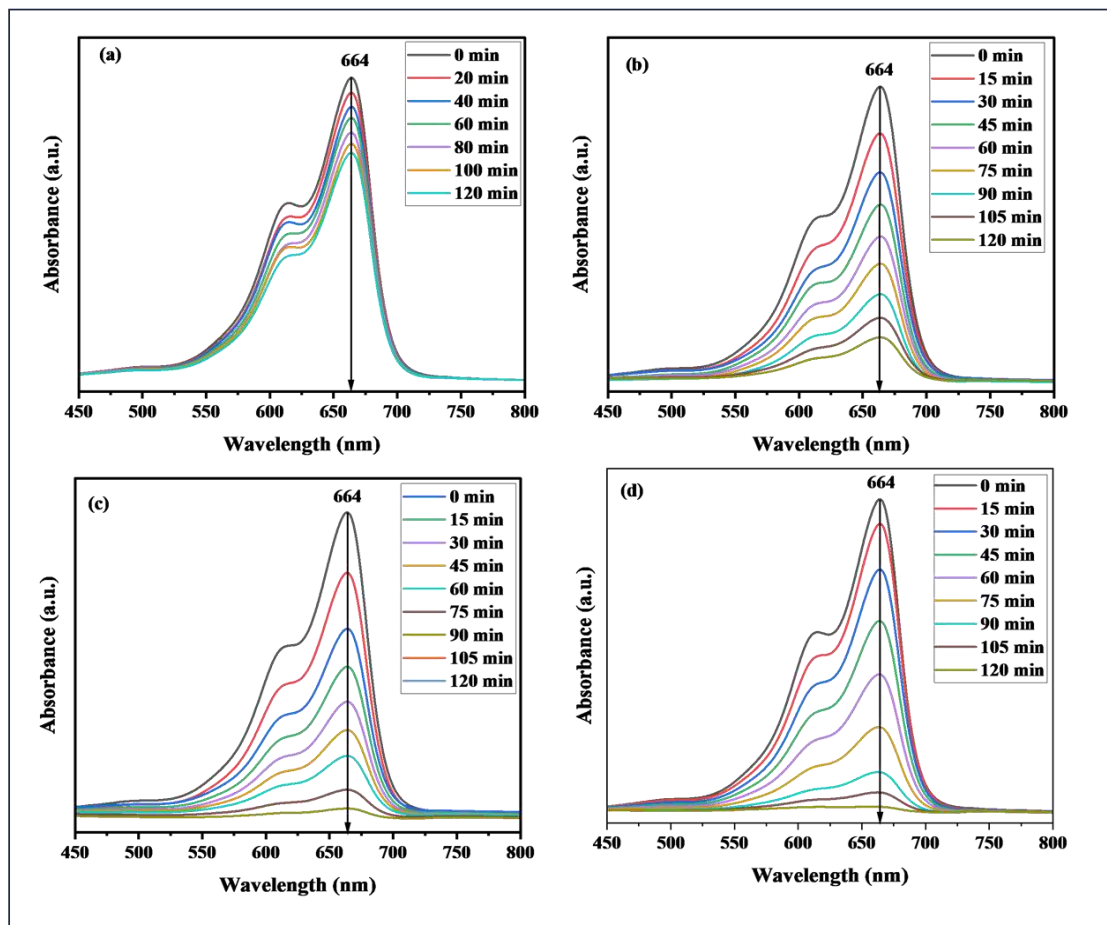


Fig. 13 : Photocatalysis of (a) MB dye, (b) CaTiO_3 , (c) Zn 3% CaTiO_3 , and (d) Zn 6 %

The samples containing Zn have higher rate constants, indicating they are better at splitting charges and absorbing light [40]. There are several synergistic motives why Zn-doped CTO has better photocatalytic activity: Firstly, Zn substitution narrows the band gap, which enhances visible-light absorption; secondly, reduced electron–hole recombination at defect sites augments charge-carrier dynamics; and finally, increased surface roughness and porosity, as witnessed in SEM analysis, generate more active reaction sites for pollutant adsorption and degradation. The concentrations of the MB solution are derived from the peak intensity of the absorbance spectra depicted in **Fig. 14**. The time-dependent photocatalytic MB degradation efficiencies of Zn-doped CTO NPs seem to be almost the same, as shown in Table 3.

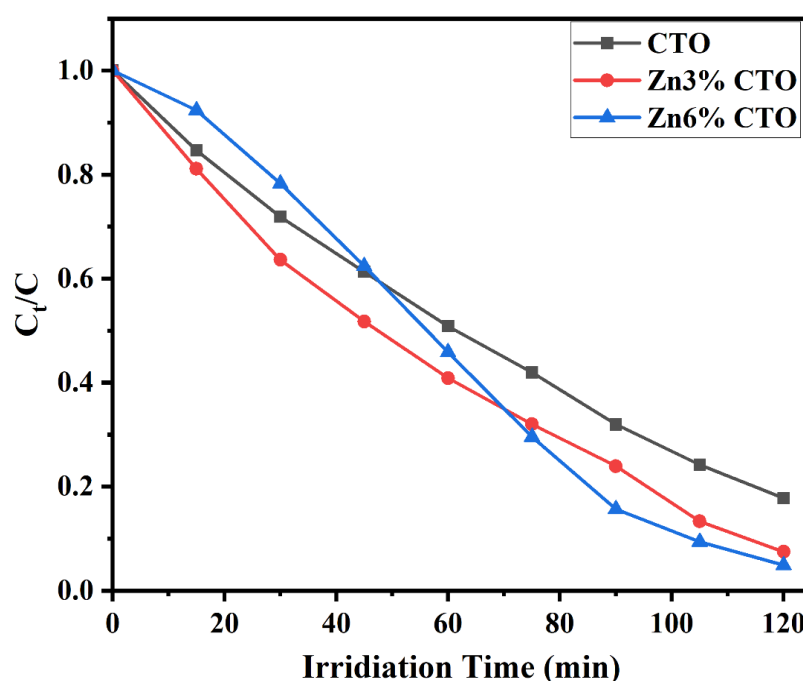


Fig. 14: (C_t/C) vs irradiation time.

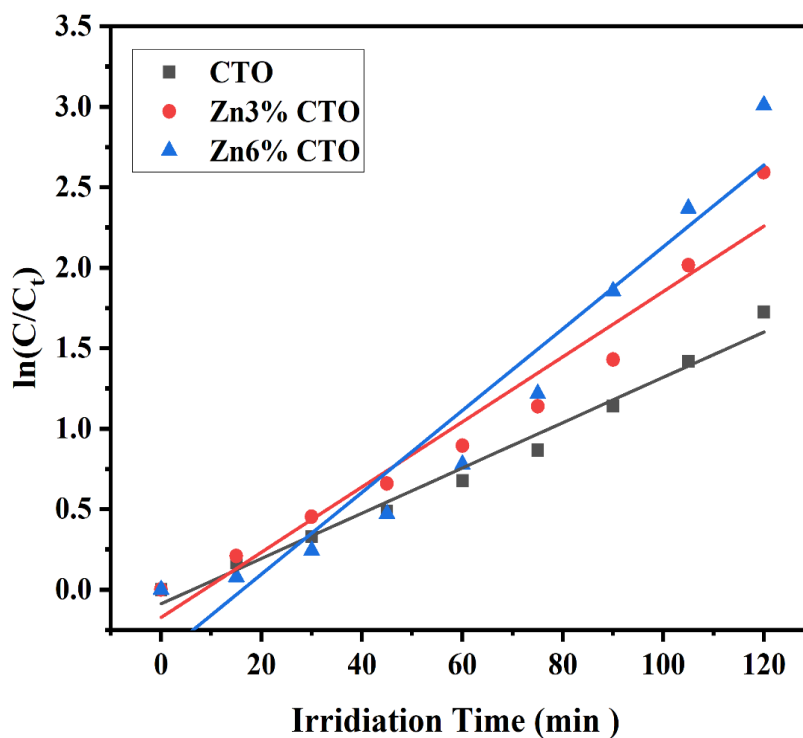


Fig. 15: $\ln(C/C_0)$ vs irradiation time.

Table 4. Encapsulation of photocatalytic results of pure and Zn-doped CaTiO_3 .

Elements	R^2	$k \text{ (min}^{-1}\text{)}$	Degradation efficiency
CaTiO_3	0.98275	0.01406	82.18
Zn 3 % CaTiO_3	0.95329	0.02025	92.48
Zn 6 % CaTiO_3	0.93568	0.02542	95.07

The CTO material has the lowest constant k of the three catalysts, indicating it requires more activation energy and the lowest degradation percentage among the materials under study. Conversely, the Zn 3% CTO and Zn 6% CTO materials exhibited the highest calculated kinetic constants, which align with the significant dye elimination observed throughout the photocatalytic process. Table 5 demonstrates a comparison of the photocatalytic activity among various catalysts.

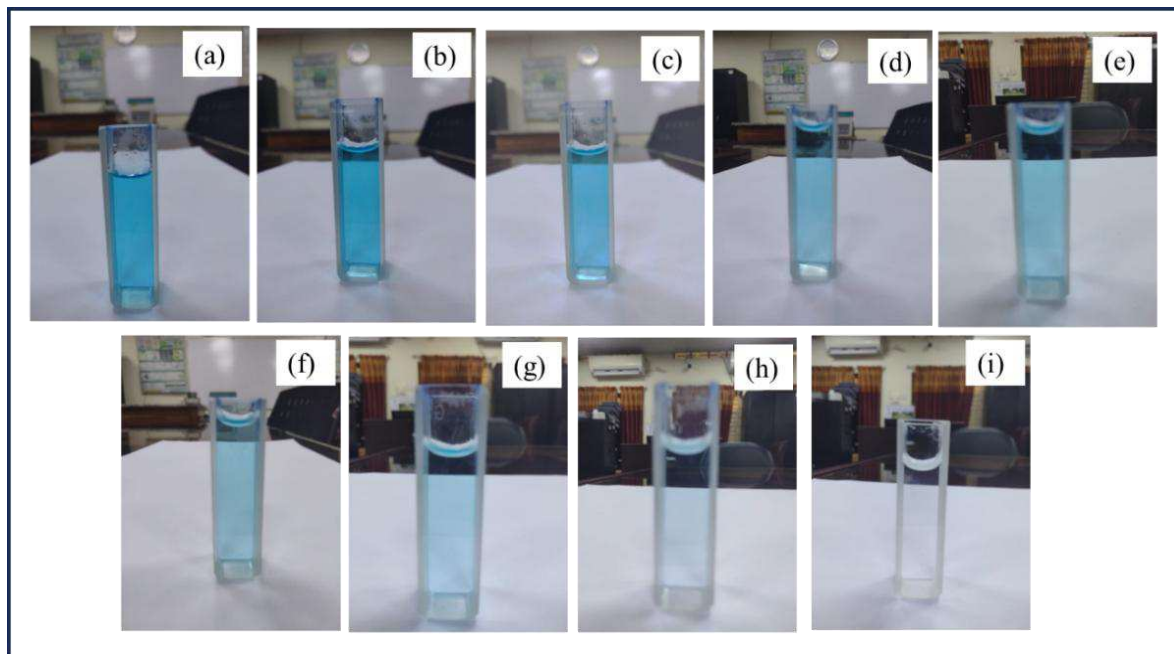


Fig. 16 : (a-i) Photocatalysis process under the UV ray over 15 min interval for Zn 6 % CaTiO_3 .

Table 5. Comparing the made photocatalyst to different catalysts

Catalyst	Degradation rate (%)	Irradiation time (min)	Ref.
Cu_2O and BiVO_4	72.9	160	[41]
$\beta\text{-MnO}_2$	90.2	120	[42]
$[\text{KNbO}_3]0.9\text{-}[\text{BaNi}_{0.5}\text{Nb}_{0.5}\text{O}_{3-\delta}]0.1$ perovskite	55	120	[43]
Ag_2S / BiVO_4 binary composite	90.2	150	[44]
Aero- TiO_2 (3D nanoarchitecture)	90	150	[45]
20 wt% Co-doped ZnFe_2O_4 (ZC_2O)	85	180	[46]
CaTiO_3 nanoparticles (CTO-NPs)	74 for 5 g/L	180	[47]
Zn 6 % doped CaTiO_3	95.07	120	This

4 Conclusions

In conclusion, Zinc-doped CaTiO_3 perovskite photocatalysts were fabricated by utilizing a solid-state reaction technique. XRD, FTIR, SEM, and UV-Vis spectroscopy were characterized comprehensively. The results established that phase-pure orthorhombic CaTiO_3 could be made, and that Zn^{2+} ions could be successfully added to the Ca^{2+} sites, precluding the formation of any secondary phases. Morphological analysis showed that adding Zn made the grains smaller and more agglomerated, with a rougher, more porous surface, thereby enhancing photocatalytic processes more effectively. Adding Zn to the material reduced the optical band gap from 3.52 eV (CTO) to 3.07 eV (Zn 6%-CTO), thereby improving light absorption in the visible region. DFT has also confirmed this bandgap reduction. This amelioration, together with flaws that trap charge and improve carrier separation, led to much improved photocatalytic activity. The Zn 6 %-CTO catalyst broke down methylene blue by 95.07 % in 120 minutes when it was subjected to UV-visible light. The undoped CTO only broke it down by 82.18%. A kinetic study showed that all processes followed pseudo-first-order kinetics. The Zn 6 %-CTO had the highest apparent rate constant ($k = 0.02542 \text{ min}^{-1}$). The improved performance of Zn-doped CTO can be attributed to the combined effects of narrowing the band gap, promoting charge delocalization, and increasing the number of active surface sites. All of these factors work together to generate reactive oxygen species ($\bullet\text{OH}$ and $\bullet\text{O}^{2-}$) that break down dyes rapidly. Compared with other published catalysts, Zn 6 %-CTO outperforms many well-known oxide photocatalysts in both competence and reaction rate. So, Zn-doped CaTiO_3 is an excellent, cost-effective, and secure photocatalyst for environmental cleanup, especially for breaking down organic contaminants when exposed to solar or visible light. Future studies might focus on combining this system with co-catalysts or forming heterojunctions to expedite charge transfer and enhance its utility in real-world wastewater treatment.

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Data Availability Statement

The datasets generated during the current study are available from the corresponding authors on a reasonable request.

Author contributions

Md. Minhajul Islam: Writing original draft, Methodology, Data collection, Data analysis; **Hridoy Roy:** Methodology, Data collection, Data analysis; **Kashfi Uddin:** Software, Theoretical Methodology, Writing theoretical portion, Data analysis; **Abdullah Al Mahmood:** Review & Editing; **Md. Bodiul Islam:** Supervision, Writing, Review & Editing; **Md. Mukter Hossain:** Software, Theoretical Methodology, Data analysis, Writing, Review & Editing.

Declarations Conflict of interest:

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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