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Ca-Doped BaCeO₃ Nanoperovskites for Enhanced Photocatalytic Degradation and Electrochemical Detection of Trimethoprim

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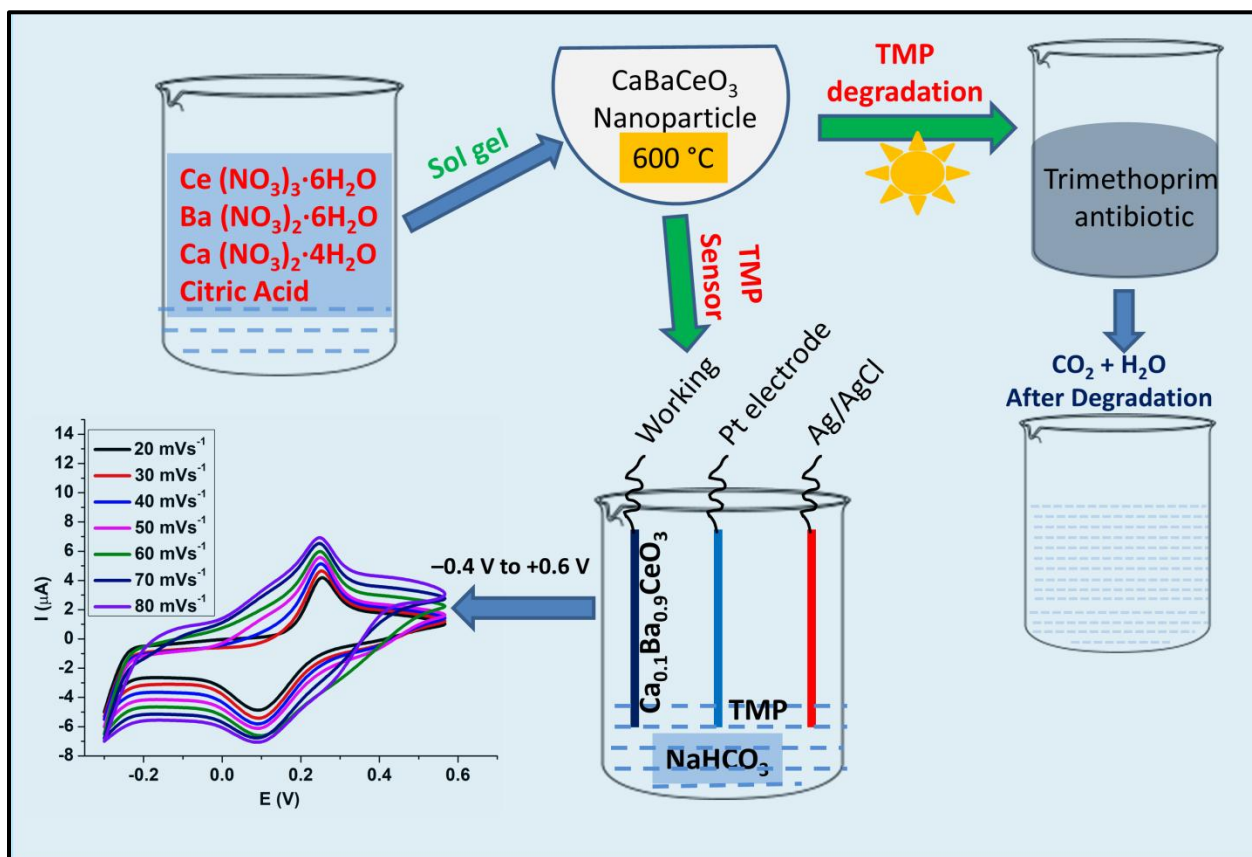
Abstract

Calcium-doped barium cerate (Ca–BaCeO₃) nanoperovskites were synthesized via a facile sol–gel method and investigated as dual-functional materials for environmental and electrochemical applications. The synthesized nanoparticles exhibited a direct optical band-gap of 2.1 eV, indicating their suitability for visible-light-driven applications. Photocatalytic activity was evaluated for the degradation of trimethoprim (TMP) under sunlight irradiation, achieving approximately 96% degradation under optimized conditions of 0.7 g L⁻¹ catalyst dosage, 35 ppm TMP concentration, pH 7, and 40 °C. The enhanced photocatalytic performance was attributed to improved charge separation and reduced electron–hole recombination resulting from Ca doping. Electrochemical sensing of TMP was investigated using cyclic voltammetry, where the modified electrode exhibited a linear response with a sensitivity of 0.5 mA μM⁻¹ cm⁻². The limit of detection (LOD) and limit of quantification (LOQ) were determined to be 0.03 μM and 0.09 μM, respectively, demonstrating reliable sensing performance. The combined photocatalytic and electrochemical performances demonstrate that Ca–BaCeO₃ nanoperovskites are promising dual-functional materials for pharmaceutical pollutant remediation and pharmaceutical sensing applications.

Keywords

Ca-doped BaCeO₃; Nanoperovskites; Sol–gel synthesis; TMP degradation; TMP sensing; Cyclic voltammetry; Photocatalysis.

Graphical Abstract



1.Introduction

Trimethoprim (TMP) is chemically referred to as 5-(3,4,5-trimethoxybenzyl) pyrimidine-2,4-diamine, widely prescribed antibiotic used to treat urinary tract, respiratory, and gastrointestinal infections, with annual consumption exceeding several thousand tons worldwide [1]. Due to its high chemical stability and low biodegradability, TMP is frequently detected in hospital effluents, wastewater treatment plant discharges, surface waters, and groundwater at concentrations ranging from ng L⁻¹ to µg L⁻¹ [2, 3]. Excessive consumption or prolonged exposure to TMP may cause adverse health effects, including gastrointestinal disturbances, hypersensitivity reactions, hematological disorders, and renal dysfunction. The continuous

release of TMP can promote the development of antibiotic-resistant bacteria and antibiotic resistance genes, posing significant ecological and public health concerns [4, 5]. Therefore, the development of efficient photocatalytic technologies for the degradation of persistent TMP contaminants has become an important research focus.

Photocatalysis has emerged as a sustainable approach for pollutant removal, with semiconductor materials achieving >90% degradation efficiency within 60–120 min through the generation of reactive oxygen species (ROS) such as $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ [6-8]. In parallel, electrochemical sensing offers rapid and sensitive detection of pharmaceutical contaminants, with detection limits often reaching the micromolar to nanomolar range (10^{-6} – 10^{-9} M) [9-11]. These dual-functional capabilities highlight the importance of developing a single material capable of integrating photocatalytic degradation, and electrochemical sensing. Nanomaterials have gained significant attention due to their high surface area, tunable electronic structure, and enhanced surface reactivity, which facilitate improved adsorption, efficient charge separation, and rapid electron transfer [12-14]. Dual-functional nanomaterials have demonstrated superior performance, achieving 90–98% pollutant degradation, and high sensing sensitivity due to synergistic interactions among their structural and surface properties [15-17]. Such integrated functionality provides a cost-effective and sustainable solution for addressing complex environmental challenges.

Among advanced materials, Perovskite oxides (ABO_3) have attracted considerable interest due to their structural flexibility and tunable physicochemical properties [18]. These materials exhibit adjustable band-gaps (typically ~ 2.0 – 3.5 eV), excellent thermal stability, and the ability to accommodate various cations, enabling defect engineering and oxygen vacancy formation [19-22]. In particular, Barium cerate (BaCeO_3) has been widely investigated for its catalytic activity and favorable electrochemical properties, making it a promising candidate for dual-functional applications [23, 24]. Doping strategies play a crucial role in enhancing the performance of perovskite materials. In this regard, substitution of Ba^{2+} with Ca^{2+} in BaCeO_3 introduces lattice distortion due to the smaller ionic radius of Ca^{2+} (~ 1.34 Å) compared to Ba^{2+} (~ 1.61 Å), leading to the formation of oxygen vacancies and defect sites [25, 26]. These structural modifications enhance electrical conductivity, promote charge carrier mobility, and suppress electron–hole recombination, thereby improving photocatalytic and electrochemical performance [27, 28].

The synthesis method also significantly influences material properties. In this study, the Sol–gel method is employed due to its advantages, including homogeneous mixing at the molecular level, controlled particle size (10–100 nm), and relatively low processing temperatures (~400–700 °C), resulting in high-purity nanostructured materials with enhanced functionality [29, 30]. Although BaCeO₃-based perovskites have been investigated for photocatalysis, fuel cells, and catalytic oxidation, their application toward simultaneous photocatalytic degradation and electrochemical sensing of pharmaceutical pollutants has rarely been explored. Furthermore, systematic investigations on the influence of Ca substitution on the electronic structure, oxygen vacancy generation, and dual-functional activity remain unavailable.

The enhanced performance of such materials can be explained through a combined mechanism. Under light irradiation, the photocatalyst generates electron–hole pairs, where photogenerated electrons reduce dissolved oxygen to form superoxide radicals (O₂^{•-}), while holes oxidize water or hydroxide ions to produce hydroxyl radicals (•OH) [31, 32]. These ROS are highly reactive and responsible for the degradation of organic pollutants into harmless products [33, 34]. Simultaneously, in electrochemical sensing, the nanomaterial facilitates efficient electron transfer between the analyte and electrode surface, enabling the oxidation of TMP producing a measurable current response [35, 36]. The presence of oxygen vacancies and enhanced conductivity further improves charge transfer kinetics, leading to superior sensing performance [37–39].

In the present work, we hypothesize that the partial substitution of Ba²⁺ with Ca²⁺ can tailor the crystal lattice, induce oxygen vacancies, narrow the optical band-gap, enhance charge transport, and thereby improve both photocatalytic and electrochemical performance. To validate this hypothesis, Ca-doped BaCeO₃ nanoperovskites were synthesized via a sol–gel method and systematically characterized. Their photocatalytic activity was evaluated through the degradation of trimethoprim (TMP), while their electrochemical sensing performance toward TMP was investigated using cyclic voltammetry and differential pulse voltammetry. To the best of our knowledge, this is the first study reporting the application of Ca-doped BaCeO₃ nanoperovskites as a dual-functional material for both photocatalytic degradation and electrochemical sensing of TMP. Furthermore, this work establishes the correlation between Ca-induced structural defects, oxygen vacancy formation, band-gap modulation, and the enhanced dual-functional

performance, highlighting the potential of Ca-doped BaCeO₃ for environmental remediation and pharmaceutical monitoring.

2. Materials and Methodology

2.1. Materials

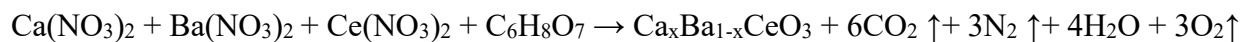
Cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.9% trace metals basis), barium nitrate [Ba(NO₃)₂, ≥99.0%], calcium nitrate tetrahydrate [Ca(NO₃)₂·4H₂O, ≥99.0%], citric acid monohydrate (C₆H₈O₇·H₂O, ≥99.5%), and ammonium hydroxide solution (NH₄OH, 25–28 wt.% NH₃ in H₂O) were purchased from Sigma-Aldrich. Distilled water was used throughout the synthesis and experimental studies. All chemicals were of analytical reagent grade and were used as received without further purification.

2.2. Methodology:

Synthesis of Ca doped BaCeO₃ nanoparticles by sol-gel method

Ca-doped BaCeO₃ nanoperovskites with nominal compositions Ca_{0.05}Ba_{0.95}CeO₃ (CBC-5), Ca_{0.1}Ba_{0.9}CeO₃ (CBC-10), and Ca_{0.2}Ba_{0.8}CeO₃ (CBC-20) were synthesized using a sol–gel combustion method. For the synthesis of CBC-10, 0.009 mol of Ba(NO₃)₂ (2.35 g), 0.001 mol of Ca(NO₃)₂·4H₂O (0.236 g), and 0.010 mol of Ce(NO₃)₃·6H₂O (4.34 g) were separately dissolved in 25 mL of distilled water. The precursor solutions were then mixed under continuous magnetic stirring to obtain a homogeneous solution. Citric acid was added as a complexing agent at a metal ion-to-citric acid molar ratio of 1:1.5 (0.030 mol, 5.76 g). The pH of the mixed solution was adjusted to 6.5–7.0 using dilute NH₄OH (25%). The solution was continuously stirred at 70–80 °C until a transparent viscous gel was obtained. The gel was dried at 110 °C for 12 h to form a xerogel. Subsequently, the xerogel underwent spontaneous combustion due to the redox reaction between nitrate ions and citric acid, producing a fluffy porous precursor powder. The obtained powder was ground thoroughly using an agate mortar and pestle and calcined at 600 °C for 4 h in ambient air with a heating rate of 5 °C min⁻¹ to obtain crystalline Ca-doped BaCeO₃ nanoparticles. The same procedure was followed for CBC-5 and CBC-20 by appropriately adjusting the molar ratio of calcium and barium precursors while maintaining the total A-site

cation concentration constant. The synthesized nanoparticles were further employed for structural characterization, photocatalytic degradation, and electrochemical sensing studies.



2.2.3. Characterization Equipment

The crystalline structure of the prepared materials was examined by X-ray diffraction (XRD) using a Rigaku Ultima III instrument with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology of the samples was evaluated by scanning electron microscopy (SEM, JEOL JSM-6390LV), and transmission electron microscopy (TEM, Hitachi H-9000 NAR) was employed to obtain detailed information on their microstructural characteristics. The optical absorption behavior of the synthesized materials was studied by UV–Vis diffuse reflectance spectroscopy (DRS) on a JASCO V-670 spectrophotometer over the wavelength range of 350–1500 nm. The corresponding band-gap energies were subsequently determined from the diffuse-reflectance data.

2.2.4. Photocatalytic Activity

The photocatalytic performance of $\text{Ca}_x\text{Ba}_{1-x}\text{CeO}_3$ was investigated for the removal of trimethoprim (TMP) from aqueous solution under natural sunlight. TMP solutions with initial concentrations between 0 and 50 ppm were prepared for the photocatalytic experiments. A predetermined amount of the photocatalyst was added to the TMP solution, and the resulting suspension was maintained under dark conditions with continuous magnetic stirring for 15–30 min to establish adsorption–desorption equilibrium. The equilibrated suspension was subsequently exposed to natural sunlight in a photocatalytic reactor while maintaining constant stirring [40]. The experiments were carried out on clear sunny days on the rooftop of the University of Mysore, Mysuru, Karnataka, India (approximately 12.18° N, 76.38° E; elevation ~575 m). The average solar irradiance at the experimental site was approximately 200 W m⁻². At selected irradiation intervals, aliquots were collected from the reaction suspension and centrifuged to remove the photocatalyst particles. The clarified solutions were analyzed using a UV–Visible spectrophotometer (Shimadzu UV-1800; 190–1100 nm), and the residual TMP concentration was determined from its absorbance at 290 nm. The effects of the major operating

parameters, including photocatalyst loading, solution pH, initial TMP concentration, and irradiation duration, were investigated systematically to determine the optimum degradation conditions. Catalyst stability and reusability were evaluated by separating the photocatalyst after each cycle, washing it thoroughly, and reusing it under the same experimental conditions. Each photocatalytic experiment was performed in triplicate. The obtained results showed good reproducibility, with the variation in degradation efficiency remaining within $\pm 3\%$.

The degradation efficiency (η) was calculated using Eq. (1):

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \quad \text{Eq..... (1)}$$

Here, C_0 and A_0 represent the initial TMP concentration and absorbance, respectively, measured prior to light exposure, whereas C_t and A_t denote the corresponding concentration and absorbance values measured after irradiation for a duration of (t). The apparent first-order rate constant (k_r) was calculated according to Eq. (2).

$$\ln \left(\frac{C_0}{C_t} \right) = k_r t \quad \text{Eq..... (2)}$$

The value of k_r was obtained from the slope of the linear relationship between $\ln (C_0/C_t)$ and irradiation time (t).

3. Results and Discussion:

3.1. XRD Pattern of $\text{Ca}_x\text{Ba}_{1-x}\text{CeO}_3$ nanoparticles

The X-ray diffraction (XRD) patterns of pure BaCeO_3 and Ca-doped BaCeO_3 are shown in **figure 1a**. Both samples exhibit well-defined diffraction peaks, indicating the successful formation of a crystalline perovskite structure. The prominent diffraction peaks observed at approximately $2\theta = 28^\circ, 31^\circ, 41^\circ, 50^\circ$, and 61° are indexed to the (002), (121), (220), (112), and (202) crystallographic planes, respectively, which are characteristic of orthorhombic BaCeO_3 and agree well with the standard JCPDS reference pattern (JCPDS No. 22-0074) [41, 42]. The Ca-doped BaCeO_3 sample exhibits diffraction peaks at nearly the same positions as those of pure BaCeO_3 , indicating that Ca^{2+} ions are successfully incorporated into the Ba^{2+} lattice sites without altering the crystal structure or forming secondary phases. The absence of additional diffraction

peaks confirms the high phase purity of the synthesized materials and suggests that no detectable impurities such as CaO, CeO₂, or BaCO₃ were formed during synthesis. A careful comparison of the diffraction patterns shows a slight shift of the diffraction peaks toward higher 2θ values in the Ca-doped sample. This shift can be attributed to the substitution of larger Ba²⁺ ions (ionic radius ≈ 1.61 Å) by smaller Ca²⁺ ions (ionic radius ≈ 1.34 Å), resulting in a slight contraction of the crystal lattice according to Bragg's law. Furthermore, the diffraction peaks of the Ca-doped sample remain sharp and intense, demonstrating that the material retains good crystallinity after doping. The slight variation in peak intensity may arise from lattice distortion and the introduction of structural defects and oxygen vacancies induced by Ca substitution. These defects can facilitate charge separation and suppress electron–hole recombination, thereby contributing to the enhanced photocatalytic and electrochemical performance observed for the Ca-doped BaCeO₃.

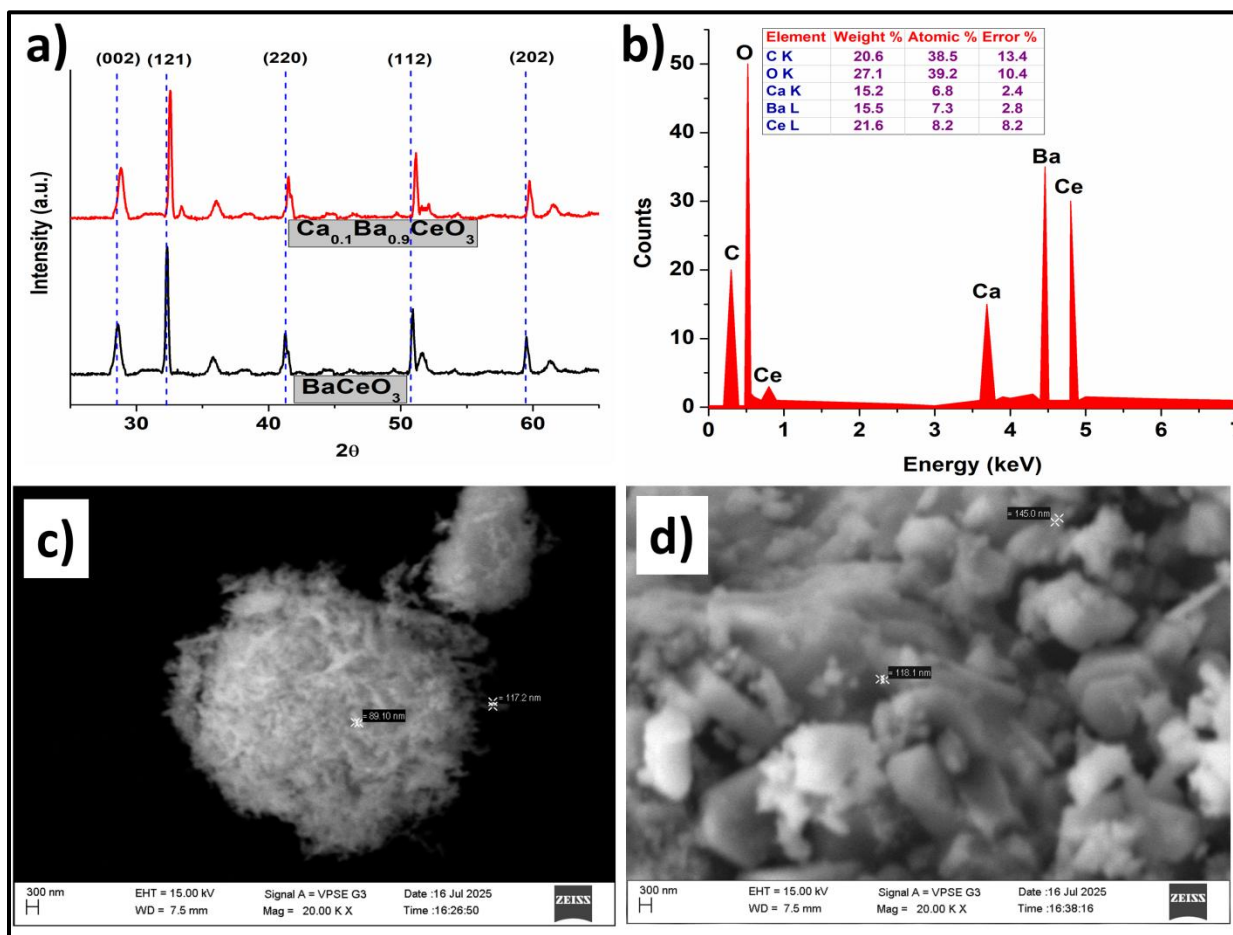


Figure 1.a): X-ray Diffraction pattern b) EDX pattern c) and d) SEM Images of Ca_{0.1}Ba_{0.9}CeO₃ nanoparticles

3.2. The Energy Dispersive X-ray Spectroscopy (EDX)

The EDX spectrum of Ca-doped BaCeO₃ nanoparticles in **figure 1b** shows distinct peaks corresponding to O (~0.52 keV), Ca (~3.7 keV), Ba (~4.4–4.6 keV), and Ce (~0.9 and ~4.8–5.0 keV), confirming the presence of all constituent elements. The clear Ca K α peak verifies the successful incorporation of Ca as a dopant in the BaCeO₃ lattice, while the relatively higher intensities of Ba and Ce peaks are attributed to their higher atomic numbers. The absence of any extra impurity-related peaks indicates high purity of the synthesized material, suggesting that Ca is incorporated into the perovskite structure rather than forming a secondary phase.

3.3. Scanning Electron Microscopy (SEM) of Ca_xBa_{1-x}CeO₃ nanoparticles

The SEM pictures of Ca_xBa_{1-x}O₃ nanoparticles at several magnifications are displayed in **figure 1c** and **1d**. An agglomerated, porous structure with a high surface area and a rough shape is shown in the images (15.0 kX, 300 nm scales), suggesting a heterogeneous distribution of nanoparticles. Nanoflower like structures may be seen emerging from clusters in the images which improved material dispersion is revealed at higher magnification. The porous nature raises the possibility of energy storage and catalytic applications. The porous/agglomerated morphology may provide increased surface accessibility, which can favor adsorption of TMP and facilitate photocatalytic reactions. The Raman, XPS survey and high-resolution spectra of the CBC-10 nanoperovskite are provided in the Supporting Information (Fig. S1 and S2), confirming the presence of the constituent elements and providing further insight into their surface chemical states.

3.4. UV DRS analysis of Ca_xBa_{1-x}CeO₃ nanoparticles

Figure 2a presents the diffuse reflectance UV–Vis absorption spectra of Ca_xBa_{1-x}CeO₃ nanoparticles. All samples exhibit strong absorption in the visible-light region, confirming their ability to utilize solar irradiation. The absorption edge of pure BaCeO₃ is observed around 560 nm, whereas Ca-substituted BaCeO₃ samples show a shift in the absorption behavior, with Ca_{0.1}Ba_{0.9}CeO₃ displaying a pronounced absorption feature near 525 nm [43]. The incorporation of Ca into the BaCeO₃ lattice modifies the electronic structure and alters the optical absorption

characteristics. The broad absorption extending throughout the visible region suggests enhanced light-harvesting capability, which is advantageous for photocatalytic applications. Furthermore, the variation in absorption edge position among the samples indicates changes in the band structure induced by Ca doping, which may influence charge carrier generation and photocatalytic performance.

3.5. Band-gap energy of $\text{Ca}_x\text{Ba}_{1-x}\text{CeO}_3$ nanoparticles

Figure 2b presents the Tauc plots of pure BaCeO_3 and $\text{Ca}_{0.1}\text{Ba}_{0.9}\text{CeO}_3$ nanoparticles, obtained from UV–Vis diffuse reflectance spectroscopy. The optical band-gap energies were estimated by extrapolating the linear region of the $(\alpha h\nu)^2$ versus $h\nu$ plots to the energy axis, assuming a direct allowed electronic transition. The optical band-gap of pristine BaCeO_3 was determined to be 2.3 eV, whereas the $\text{Ca}_{0.1}\text{Ba}_{0.9}\text{CeO}_3$ nanoparticles exhibited a reduced band-gap of 2.1 eV. The observed band-gap narrowing is attributed to the incorporation of Ca^{2+} ions into the BaCeO_3 lattice, which induces lattice distortion and modifies the electronic band structure. The substitution of the smaller Ca^{2+} ions for Ba^{2+} generates localized defect states and oxygen vacancies, leading to the formation of intermediate energy levels within the forbidden band. These defect states effectively reduce the energy required for electronic excitation from the valence band to the conduction band, resulting in enhanced visible-light absorption [44]. The reduced band-gap significantly improves the photocatalytic response of the Ca-doped sample by enabling the utilization of a broader portion of the solar spectrum. Moreover, the oxygen vacancies and defect states introduced by Ca doping act as effective charge-trapping centers, suppressing the recombination of photogenerated electron–hole pairs and prolonging the lifetime of charge carriers. Consequently, a greater number of electrons and holes participate in the generation of reactive oxygen species such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\text{O}_2^{\bullet-}$), which are responsible for the degradation of trimethoprim. As a result, the $\text{Ca}_{0.1}\text{Ba}_{0.9}\text{CeO}_3$ nanoparticles exhibited excellent photocatalytic activity, achieving approximately 96% degradation of trimethoprim under light irradiation. Therefore, the enhanced photocatalytic performance is attributed to the combined effects of band-gap narrowing, improved visible-light absorption, efficient charge separation, and increased oxygen-vacancy concentration induced by Ca doping.

3.6. Photocatalytic degradation of TMP

Figure 2c shows the photocatalytic degradation of trimethoprim (TMP) over pure BaCeO₃ and Ca-doped BaCeO₃ photocatalysts under light irradiation. The degradation efficiency increases with irradiation time for all samples, indicating the progressive decomposition of TMP through photocatalytic reactions. Among the investigated photocatalysts, Ca_{0.1}Ba_{0.9}CeO₃ exhibited the highest photocatalytic performance, achieving approximately 96% degradation within 45 min. In comparison, Ca_{0.2}Ba_{0.8}CeO₃ and Ca_{0.05}Ba_{0.95}CeO₃ showed slightly lower degradation efficiencies of about 95%, while pure BaCeO₃ reached only about 90% degradation under identical conditions. The enhanced photocatalytic activity of the Ca-doped samples can be attributed to the incorporation of Ca²⁺ ions into the BaCeO₃ lattice, which modifies the electronic structure and promotes efficient separation of photogenerated electron–hole pairs [45]. In particular, the Ca_{0.1}Ba_{0.9}CeO₃ composition appears to provide an optimal doping concentration, resulting in an increased number of surface-active sites and defect centers that facilitate charge transfer and reactive oxygen species generation. The superior performance of this sample suggests that an appropriate amount of Ca doping effectively suppresses charge carrier recombination and enhances photocatalytic reactions. However, further increasing the Ca content to $x = 0.2$ does not significantly improve the degradation efficiency, indicating that excessive doping may not provide additional benefits and could introduce recombination centers.

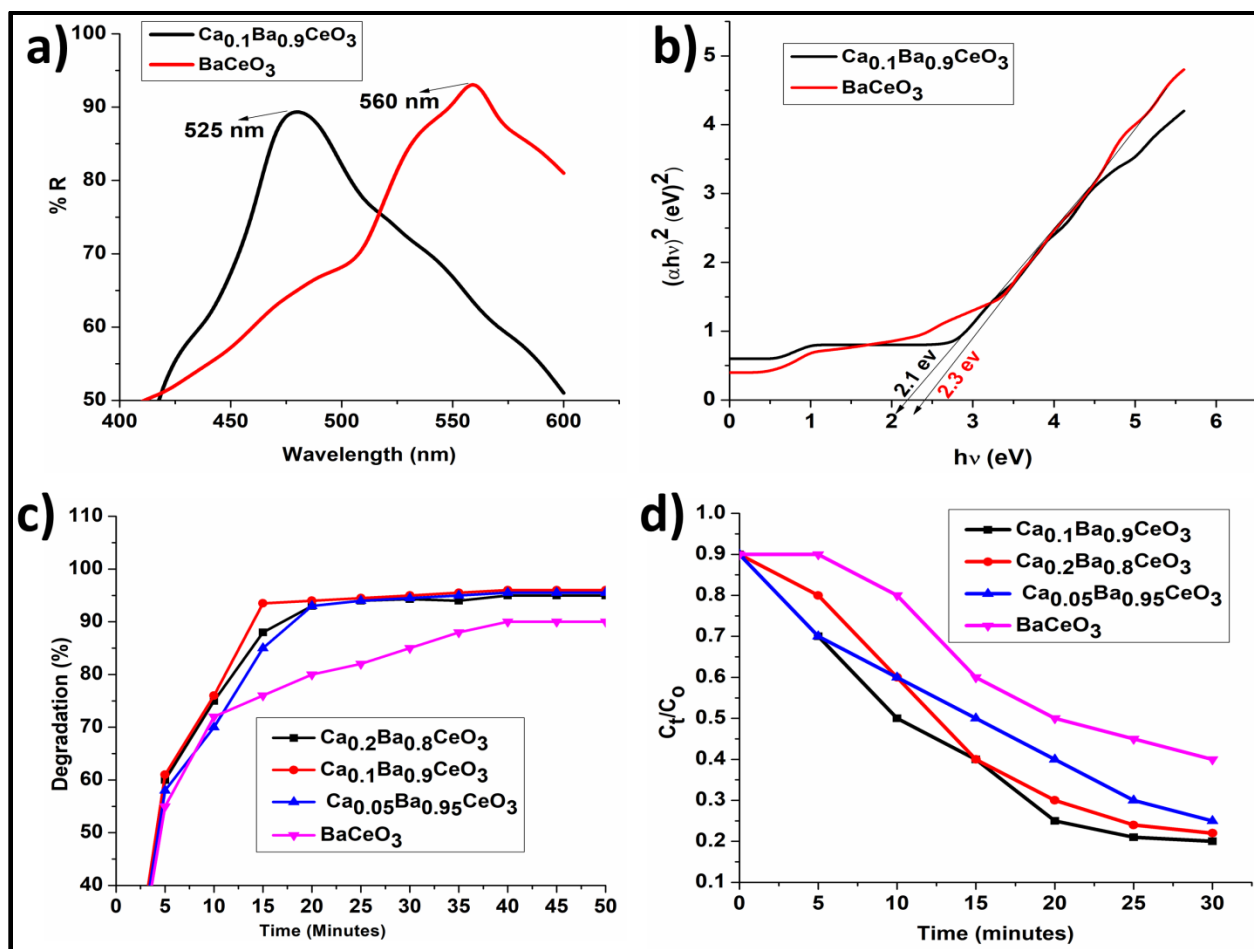


Figure 2.a): UV-Vis diffuse reflectance spectra b) Tauc plots of CBC 10 nanoparticles c) and d) Photocatalytic degradation of TMP

3.7. Normalized TMP concentration (C_t/C_0) versus irradiation time:

Figure 2d depicts the temporal change in the normalized concentration (C_t/C_0) of trimethoprim during photocatalytic degradation over pure BaCeO₃ and Ca-doped BaCeO₃ photocatalysts. For all samples, the C_t/C_0 value decreases progressively with increasing irradiation time, indicating continuous degradation of TMP. Among the investigated photocatalysts, Ca_{0.1}Ba_{0.9}CeO₃ exhibits the most rapid decline in C_t/C_0 , reaching a value of approximately 0.20 after 30 min, which corresponds to nearly 96% degradation of TMP. In contrast, pure BaCeO₃ shows the slowest degradation rate, retaining a C_t/C_0 value of about 0.40 after the same irradiation period. The enhanced degradation performance of the Ca-doped samples demonstrates the beneficial effect

of Ca incorporation on photocatalytic activity. The improved efficiency can be attributed to enhanced charge carrier separation, increased surface-active sites, and the formation of defect states that facilitate the generation of reactive oxygen species. Among the doped compositions, $\text{Ca}_{0.1}\text{Ba}_{0.9}\text{CeO}_3$ provides the optimum doping concentration, resulting in the highest photocatalytic degradation rate. These results confirm that an appropriate level of Ca doping significantly enhances the photocatalytic degradation of trimethoprim.

3.8. Transmission Electron Microscope (TEM) Images

The TEM images of sol–gel synthesized CBC 10 nanoparticles reveal the nanoscale morphology and particle size distribution of the material. In **Figure 3a**, the low-magnification TEM image shows the formation of nearly spherical to irregular nanoparticles with noticeable agglomeration, which is commonly observed for sol–gel derived oxide nanoparticles due to their high surface energy and calcination-induced particle–particle interactions. The particles are uniformly distributed, and their sizes are in the nanometer range, as indicated by the 20 nm scale bar. In **Figure 3b** the high-resolution TEM image provides a closer view of individual nanoparticles, showing well-defined particle boundaries. The measured particle sizes are approximately 19–29 nm, confirming the nanoscale nature of the CBC 10. The relatively uniform size and compact morphology suggest effective nucleation and growth during the sol–gel process. Overall, the TEM analysis confirms the successful formation of Ca-doped BaCeO_3 nanoparticles with nanoscale dimensions, which is beneficial for enhanced surface area and improved photocatalytic performance.

3.9. BET Surface Area Analysis

The specific surface areas of pristine BaCeO_3 and Ca-doped BaCeO_3 (CBC 10) were evaluated from nitrogen adsorption–desorption measurements conducted at 77 K using a NOVA 3200 BET surface area analyzer (Quantachrome Corporation, USA). Before measurement, the samples were degassed under vacuum at 300 °C for 3 h to eliminate physically adsorbed moisture and other volatile species from the surface. The specific surface area was subsequently calculated using the Brunauer–Emmett–Teller (BET) model [46]. Pore-size distribution was not determined by the Barrett–Joyner–Halenda (BJH) method in this study. The corresponding nitrogen adsorption–desorption isotherms of BaCeO_3 and CBC 10 are presented in **Fig. 3c**. Both samples

exhibit type IV isotherms accompanied by H3 hysteresis loops, indicating the presence of mesoporous features. CBC 10 possesses a comparatively larger specific surface area of $175 \text{ m}^2 \text{ g}^{-1}$, whereas pristine BaCeO_3 exhibits a value of $150 \text{ m}^2 \text{ g}^{-1}$. The difference in surface area may be associated with changes in the surface and porous characteristics induced by Ca incorporation during material formation. The relatively high surface area of CBC 10, together with its mesoporous characteristics, provides a greater accessible surface for interaction with the aqueous phase. These features can facilitate the adsorption of TMP molecules and increase the availability of surface-active sites during photocatalysis. In combination with the modified structural and optical properties of the Ca-doped material, the enhanced surface area may contribute to improved photocatalytic performance by providing a larger reaction interface between the catalyst, pollutant molecules, and the surrounding solution.

3.10. Rate Constant and order of photodegradation reaction

The degradation kinetics of TMP over the photocatalyst was analyzed using a pseudo-first-order kinetic approach, which is widely employed to describe the photocatalytic removal of dilute organic contaminants [47]. The corresponding kinetic expression is given in Eq. (1):

where (C) denotes the concentration of TMP at a given irradiation time and k_{app} is the apparent first-order rate constant (min^{-1}). Upon integration of Eq. (1), with $C_t = C_0$ at $t = 0$ and $(C=C_t)$ at irradiation time (t), the following linearized expression is obtained:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{\text{app}} t \dots\dots\dots \text{Eq. 2}$$

where (C_0) and (C_t) correspond to the initial TMP concentration and the concentration remaining after irradiation for time (t), respectively. The contribution of direct photolysis was examined through a control experiment performed without the photocatalyst. No appreciable decrease in TMP concentration was observed even after 2 h of sunlight irradiation, indicating that direct photolysis made a negligible contribution to TMP removal under the experimental conditions. The (k_{app}) values were obtained from the slopes of the linear plots of $\ln(C_0/C_t)$ against irradiation time, as presented in **Fig. 3d**. Among the investigated pH conditions, the experimental data showed the best linear correlation with the pseudo-first-order model at pH 7. The corresponding k_{app} reached $4.43 \times 10^{-2} \text{ min}^{-1}$, indicating that pH 7 provided the most favorable conditions for photocatalytic TMP degradation among the conditions examined.

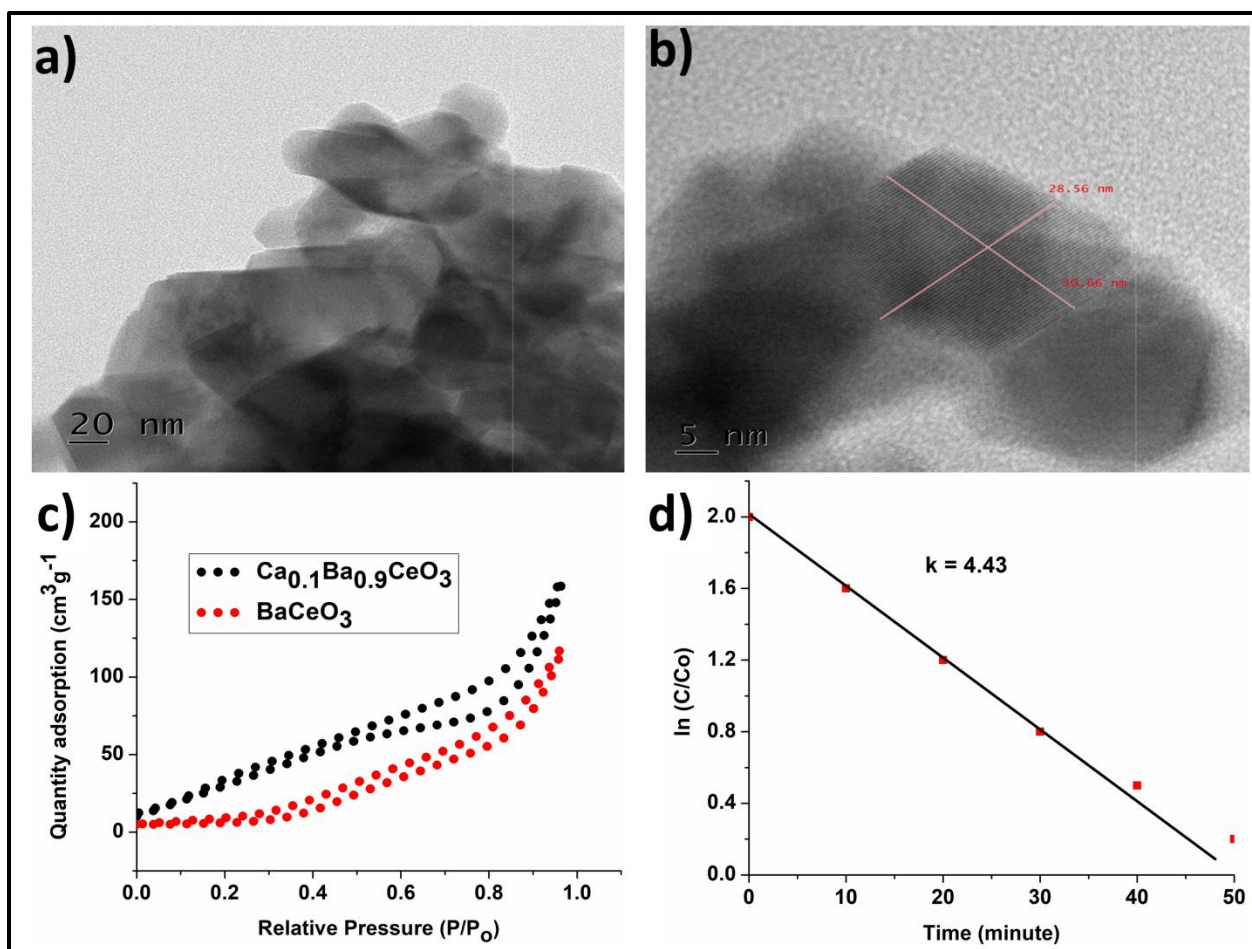


Figure 3. a) and b) TEM images of Photocatalyst $\text{Ca}_{0.1}\text{Ba}_{0.9}\text{CeO}_3$ Concentration c) BET surface area and d) rate constant on degradation

3.11. Effect of Photocatalyst CBC 10 Concentration

The **Figure 4c** shows TMP degradation efficiency which increased significantly with increasing catalyst dosage from 0.3 to 0.7 g L^{-1} , reaching a maximum degradation efficiency of approximately 96%. The improvement can be attributed to the increased availability of active surface sites and enhanced generation of reactive oxygen species due to the larger number of photocatalytically active particles. Beyond 0.7 g L^{-1} , the degradation efficiency remained nearly constant, indicating that the optimum catalyst loading had been achieved. Further addition of catalyst did not enhance degradation because excessive catalyst particles can cause light scattering and shielding effects, reducing photon penetration into the reaction medium.

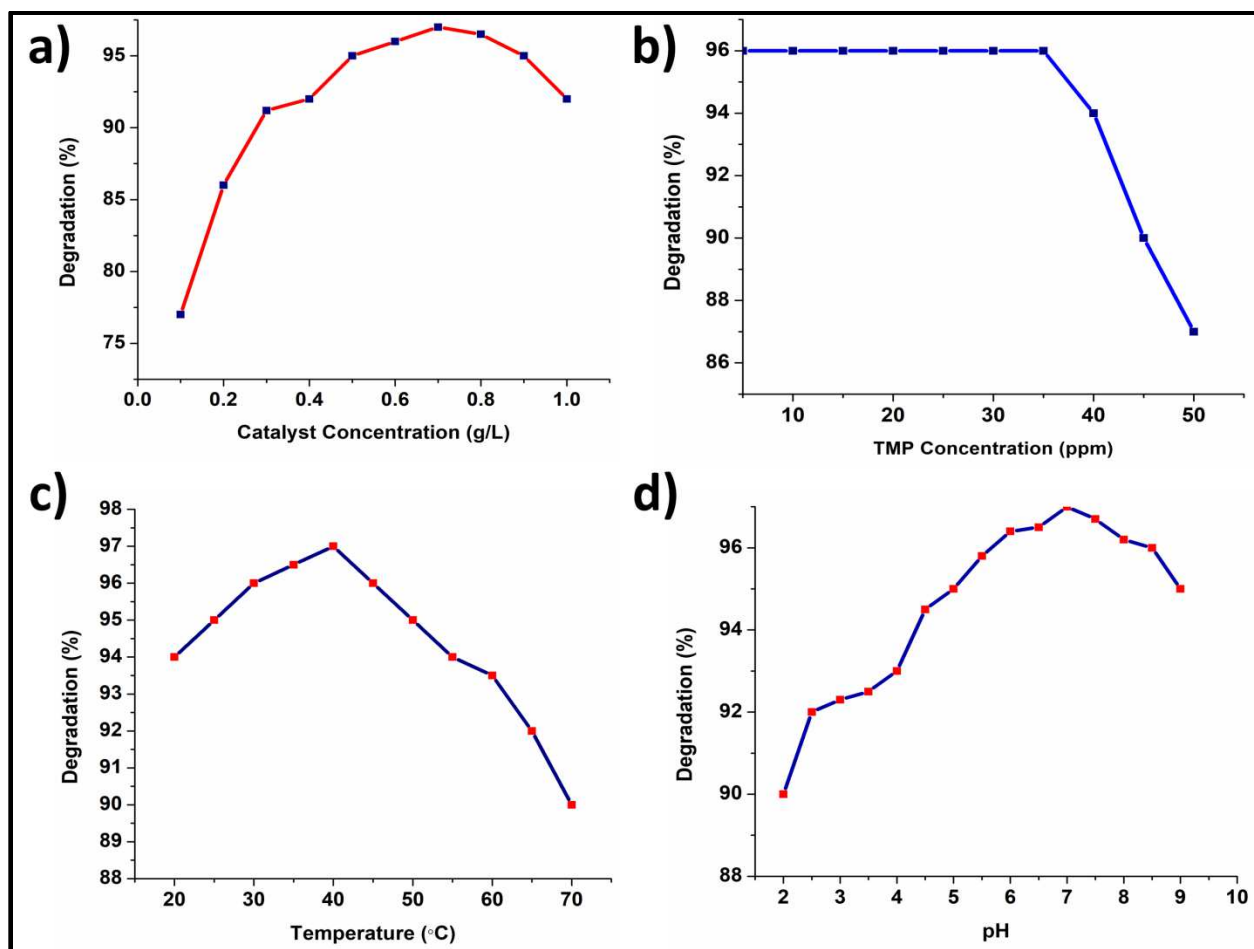


Figure 4. Effect of a): Photocatalyst CBC 10 Concentration b) TMP concentration c) Temperature and d) pH on degradation

3.12. Effect of initial TMP concentration

Figure 4b shows the effect of TMP concentration on photocatalytic degradation. The degradation efficiency gradually decreased with increasing TMP concentration from 5 to 50 ppm. At lower concentrations, the number of pollutant molecules is relatively small compared to the available active sites, resulting in efficient degradation. As the TMP concentration increases, more pollutant molecules compete for the same active sites, while the solution becomes increasingly opaque, limiting light penetration and reducing the generation of reactive species. Consequently, the degradation efficiency decreased from approximately 96% at low concentrations to about 91% at 50 ppm.

3.13. Effect of Temperature

Figures 4c illustrate how temperature affects the degradation of TMP by varying temperature from 20 to 70 °C. The figure suggests that the degradation efficiency increased steadily with increasing reaction temperature from 20 to 40 °C, reaching approximately 96%. The enhanced degradation at elevated temperatures may be attributed to improved mass transfer, increased diffusion of reactant molecules toward the catalyst surface, and accelerated photocatalytic reaction kinetics. Higher temperatures facilitate the interaction between TMP molecules and reactive oxygen species, thereby promoting degradation. As the temperature increases, fewer ROS species, such as superoxide and hydroxyl radicals, will be produced. The impact of sunlight irradiation on TMP is another explanation for this result. At high temperature, a considerable amount of light may be absorbed by the TMP molecules instead of the photocatalyst, which lowers the production of $\bullet\text{OH}$ and O_2^- radicals and the photocatalytic activity.

3.14. Effect of pH

The effect of solution pH on TMP photocatalytic degradation was investigated over the pH range of 2–12, and the corresponding degradation profiles are shown in **Fig. 4d**. The degradation efficiency increased progressively from acidic conditions toward neutral pH, reaching approximately 96% at pH 7. This behavior can be associated with changes in the photocatalyst surface charge, TMP protonation state, and the availability of reactive species during irradiation. Under strongly acidic conditions, catalyst–TMP interactions and reactive-species formation may be less favorable, resulting in lower degradation efficiency. The maximum activity at pH 7 suggests favorable adsorption and interfacial charge-transfer conditions. At pH values above 7, a slight decrease in degradation was observed, which may arise from changes in surface charge, TMP speciation, and reactive-species stability. Thus, pH 7 was identified as the optimum condition among those examined.

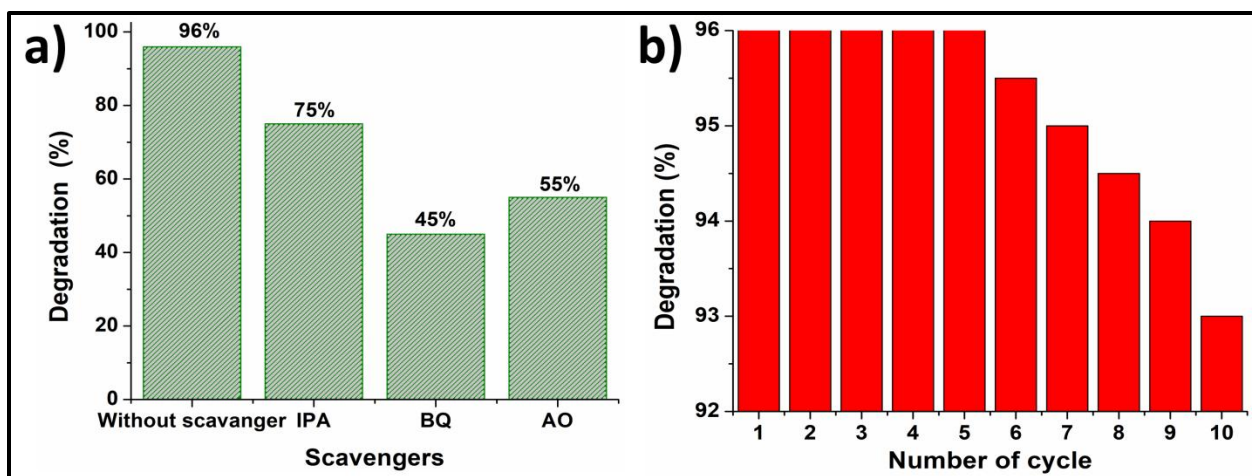


Figure 5.a) Radical Scavenger test of CBC 10, b) Catalyst CBC 10 reusability on TMP degradation

3.15. Radical-Scavenging analysis

To elucidate the contribution of different reactive oxygen species (ROS) in the photocatalytic degradation of TMP, radical scavenging experiments were carried out using specific quenchers. Isopropanol (IPA, 1 mM), benzoquinone (BQ, 1 mM) and ammonium oxalate (AO, 1 mM) were employed as scavengers for $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and h^+ respectively. As illustrated in **figure 5a**, the degradation efficiency decreased from 96% in the absence of scavengers to 75% with IPA, 45% with BQ and 55% with AO. However, the degradation efficiency dramatically decreased to about 45% upon the addition of benzoquinone, a known quencher for hydroxyl ($\text{O}_2^{\bullet-}$) radicals. The pronounced decrease in degradation efficiency in the presence of BQ indicates a major contribution from superoxide radicals ($\bullet\text{O}_2^-$), while the inhibition observed with IPA and AO suggests additional contributions from hydroxyl radicals and photogenerated holes

3.16. Catalyst reusability/cycle performance

The $\text{Ca}_{0.1}\text{Ba}_{0.9}\text{CeO}_3$ nanoparticles exhibited good recyclability, retaining approximately 96% TMP degradation efficiency after five consecutive photocatalytic cycles (**Fig. 5b**). The minimal loss in activity upon repeated use indicates satisfactory catalyst stability and supports its potential for practical and repeated photocatalytic applications. This aspect has been clarified in the revised manuscript.

3.17. Mechanism of Photocatalytic Degradation by CBC 10 Nanoparticles

Under natural sunlight, CBC 10 is activated when the incident photon energy is sufficient to promote electrons from the valence band (VB) to the conduction band (CB), leaving positively charged holes (h^+) in the VB. The introduction of Ca^{2+} into the $BaCeO_3$ lattice can induce structural distortion and facilitate the formation of oxygen vacancies, which may serve as trapping sites for charge carriers and thereby reduce electron–hole recombination (**Fig. 6**). The photogenerated electrons can subsequently interact with dissolved O_2 at the catalyst surface to generate superoxide radicals ($\bullet O_2^-$), whereas the holes can participate in the oxidation of surface-bound H_2O or OH^- to produce hydroxyl radicals ($\bullet OH$) [48]. The resulting reactive oxygen species can attack TMP molecules and promote the breakdown of their molecular structure, ultimately leading to further oxidation and mineralization into smaller and less harmful products, including CO_2 , H_2O , and inorganic species. The maximum degradation of approximately 96% obtained at pH 7, a catalyst loading of 0.7 g per 100 mL, an initial TMP concentration of 35 ppm, and a temperature of 40 °C can be associated with favorable catalyst–pollutant interactions, sufficient availability of active sites, effective light utilization, and enhanced reaction kinetics. Overall, Ca incorporation is proposed to improve the photocatalytic performance of $BaCeO_3$ by modifying its structural and surface characteristics and facilitating more effective separation and utilization of photogenerated charge carriers under sunlight irradiation.

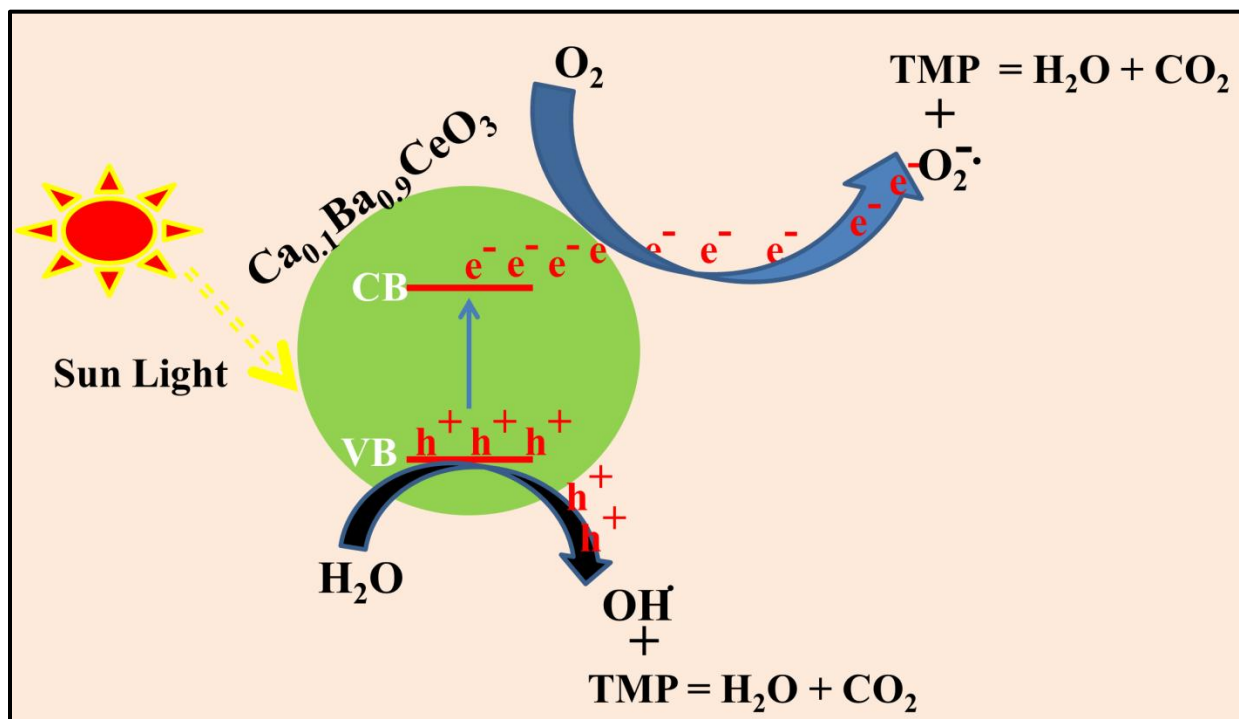


Figure 6: Schematic Mechanism of TMP degradation using $\text{Ca}_{0.1}\text{Ba}_{0.9}\text{CeO}_3$ nanoparticles

Table 1: Comparison table of degradation of TMP with different photocatalyst

Sl No	Photocatalyst	Light Source	Degradation Efficiency (%)	Time (min)	Reference
1	AgBr/h-MoO ₃	Visible Light	~93%	60	[49]
2	g-C ₃ N ₄ /AgMoO ₄	Visible light	~91%	60	[50]
3	Ag–AgCl/WO ₃ /g-C ₃ N ₄	Visible light	99.9%	60	[51]
4	NiFe ₂ O ₄ @MoO ₃	UV light	~88%	70	[52]
5	Ca _{0.1} Ba _{0.9} CeO ₃ (CBC 10)	Sunlight	~96%	45	Present work

Table 1 presents a comparison of the photocatalytic degradation performance of CBC 10 with previously reported photocatalysts for trimethoprim removal. The synthesized CBC 10 nanoperovskite achieved approximately 96% degradation within 45 min under sunlight irradiation. This performance is superior to that of AgBr/h-MoO₃ (93%), g-C₃N₄/AgMoO₄ (91%), and NiFe₂O₄@MoO₃ (88%) reported in the literature. Although Ag–AgCl/WO₃/g-C₃N₄ exhibited a slightly higher degradation efficiency of 99.9%, it required a more complex heterostructure. The enhanced photocatalytic activity of CBC 10 can be attributed to Ca-induced lattice distortion, improved charge separation, and reduced electron–hole recombination. Furthermore, the catalyst demonstrated high degradation efficiency within a shorter reaction time under natural sunlight. These results indicate that CBC 10 is an efficient and cost-effective photocatalyst for the degradation of pharmaceutical pollutants in wastewater.

4. Electrochemical Studies

The CBC-10 modified working electrode was prepared by a simple drop-casting technique using carbon paper as the electrode substrate. Briefly, 5 mg of CBC-10 nanocomposite was suspended in 1 mL of an isopropanol/deionized-water mixture (1:1, v/v) and sonicated for 20 min to obtain a homogeneous dispersion. Subsequently, 50 μL of Nafion solution (5 wt.%) was introduced as a binding agent, and the suspension was sonicated further to ensure uniform distribution of the

catalyst. The resulting catalyst ink was deposited onto pre-cleaned carbon paper by drop casting. A volume of 100 μL was used for an electrode area of 1.0 cm^2 , whereas 50 μL was applied for a 0.5 cm^2 electrode. The coated electrodes were dried at 60 $^{\circ}\text{C}$ for 30 min. Electrical connection was established by attaching a copper wire to the carbon-paper substrate using conductive silver paste. Electrochemical measurements were performed in a conventional three-electrode cell, with the CBC-10-coated carbon paper serving as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. Cyclic voltammetry measurements were carried out in aqueous 0.5 M NaHCO_3 electrolyte at room temperature ($\text{pH} \approx 7.3$).

4.1. Electrochemical characteristics of the BaCeO_3 , CBC 5, CBC 10, and CBC 20 electrodes.

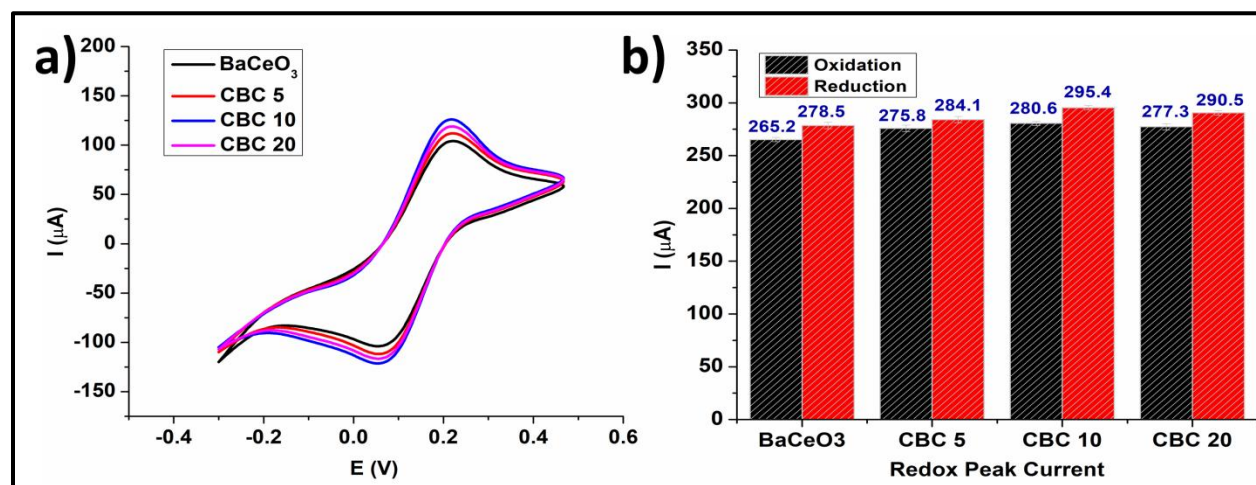


Figure 7. (a) Cyclic voltammetry (CV) curves (b) the bar diagram of the oxidation/reduction peak currents of the photocatalysts in 20 μM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution containing 0.1 M KCl at a scan rate of 70 mVs^{-1}

The electrochemical characteristics of the BaCeO_3 , CBC 5, CBC 10, and CBC 20 modified electrodes were investigated by cyclic voltammetry (CV) using the reversible redox couple $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ as the electrochemical probe [53]. **Figure 7a** shows the CV curves recorded in 5 mM $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ containing 0.1 M KCl at a scan rate of 80 mV s^{-1} . All electrodes exhibit well-defined anodic and cathodic peaks, confirming the reversible one-electron redox reaction of the ferri/ferrocyanide couple. Compared with pristine BaCeO_3 , the Ca-doped electrodes exhibited enhanced redox responses, indicating improved electron transfer

kinetics after Ca incorporation. Among the investigated samples, the CBC 10 electrode demonstrated the highest anodic and cathodic peak currents of 280.6 and 295.4 μA , respectively, which are significantly higher than those of CBC 5 (275.8 and 284.1 μA), CBC 20 (277.3 and 290.5 μA), and pristine BaCeO_3 (255.2 and 278.5 μA). The superior electrochemical performance of CBC 10 can be attributed to its optimized Ca concentration, which facilitates faster charge transport and increases the number of electroactive sites, thereby enhancing the overall electron transfer process. The comparative peak current values are summarized in **Figure 7b**.

4.2. Electrochemical behavior of trimethoprim at BaCeO_3 , CBC 5, CBC 10, and CBC 20 modified electrodes

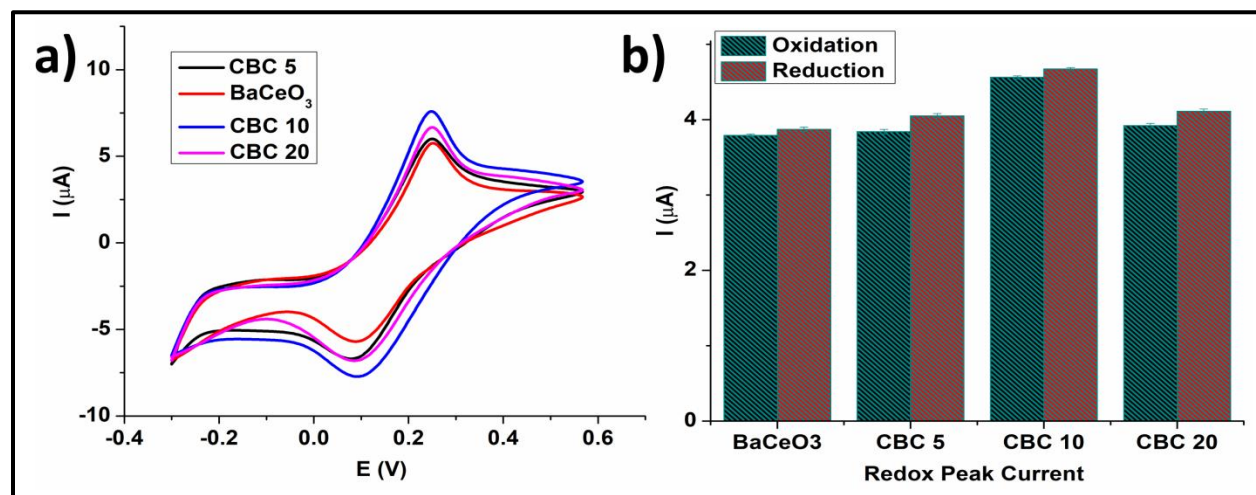


Figure 8. (a) CV response of modified electrodes (b) the bar diagram of redox peak currents of 20 μM TMP in 0.1 M PBS (pH 8). The scan rate of CV is 80 mV s^{-1}

The electrochemical sensing performance of BaCeO_3 , CBC 5, CBC 10, and CBC 20 modified electrodes toward trimethoprim (TMP) was evaluated by cyclic voltammetry (CV) in 0.1 M phosphate buffer solution (PBS, pH 8) containing 20 μM TMP at a scan rate of 80 mV s^{-1} . The corresponding CV responses are presented in **Figure 8a**. All modified electrodes exhibited well-defined oxidation and reduction peaks, confirming their electrochemical activity toward TMP. A comparison of the electrochemical parameters reveals that the CBC 10 electrode possesses superior electrocatalytic performance among the investigated samples. The anodic peak potential

(E_{pa}) of CBC 10 was observed at 252.5 mV, which is significantly lower than those of pristine BaCeO₃ (281.4 mV), CBC 5 (277.6 mV), and CBC 20 (271.8 mV). The lower oxidation potential indicates that TMP oxidation occurs more readily on the CBC 10 surface, requiring a reduced overpotential and demonstrating faster electron transfer kinetics.

Furthermore, the CBC 10 electrode exhibited the highest anodic and cathodic peak currents of 4.59 μ A and 4.55 μ A, respectively, compared with CBC 5 (4.12 and 3.92 μ A), CBC 20 (3.82 and 3.78 μ A), and pristine BaCeO₃ (3.56 and 3.24 μ A), as summarized in **Figure 8b**. The enhanced current response of CBC 10 can be attributed to the optimized Ca doping level, which promotes electrical conductivity, increases the number of electroactive sites, and facilitates efficient charge transfer at the electrode–electrolyte interface [54]. In contrast, excessive Ca incorporation (CBC 20) may introduce structural defects or agglomeration, leading to a slight decline in electrochemical performance. The cathodic peak potentials (E_{pc}) remained nearly unchanged for all electrodes, indicating that the improved sensing behavior primarily arises from the enhanced anodic oxidation of TMP rather than changes in the reduction process. These findings demonstrate that the CBC 10 modified electrode provides the most favorable electrochemical characteristics for TMP detection, owing to its accelerated electron transfer kinetics and superior electrocatalytic activity.

4.3. Effect of scan rate on Determination of Trimethoprim:

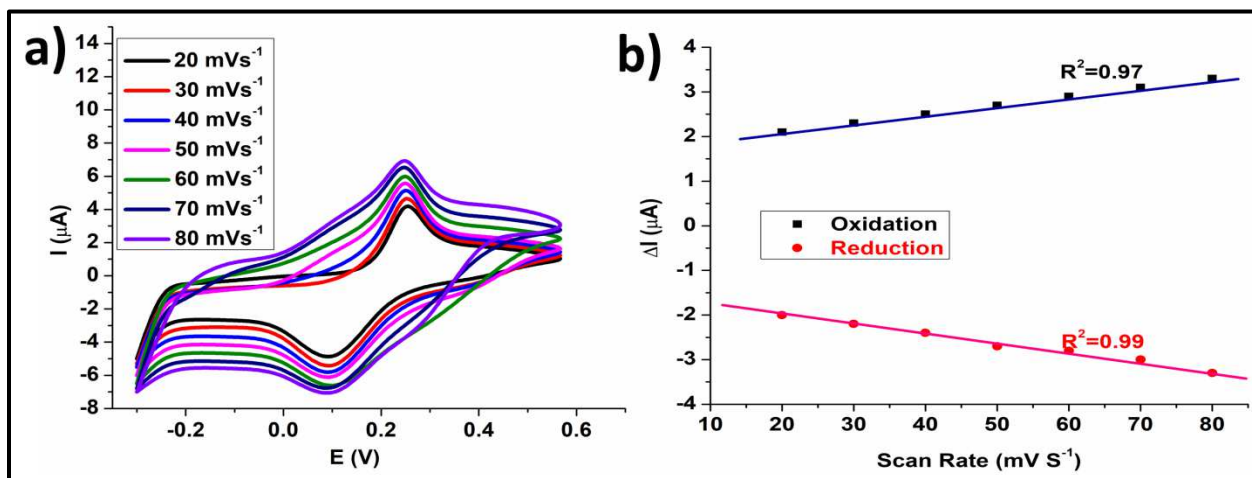


Figure 9. (a) Cyclic voltammetry (CV) curves of CBC 10 modified electrode in 0.1 M PBS (pH 8) containing 20 μM trimethoprim at different scan rates (b) Linear relationship between peak current and scan rate indicating surface-controlled electrochemical behavior.

Figure 9a shows the cyclic voltammograms (CVs) of the CBC 10 modified electrode recorded in 0.1 M PBS (pH 8) containing 20 μM trimethoprim (TMP) at scan rates ranging from 20 to 80 mV s^{-1} . Both the anodic and cathodic peak currents increase progressively with increasing scan rate while maintaining nearly identical peak shapes, indicating a fast and stable electrochemical process. The potential shifts with increasing scan rate indicate kinetic limitations and suggest an irreversible/quasi-irreversible electrochemical process. The enhanced current response at higher scan rates confirms efficient electron transfer and excellent electrocatalytic activity of the CBC 10 electrode toward TMP oxidation [55]. **Figure 9b** presents the relationship between the oxidation and reduction peak currents and the scan rate. Both anodic and cathodic peak currents exhibit an excellent linear correlation with scan rate, with correlation coefficients of $R^2 = 0.97$ and $R^2 = 0.99$, respectively. This linear dependence indicates that the electrochemical oxidation of TMP at the CBC 10 modified electrode is predominantly a surface-controlled (adsorption-controlled) process, where TMP molecules are adsorbed onto the electrode surface before undergoing electron transfer. The high linearity also demonstrates the good electrochemical stability, reproducibility, and rapid charge-transfer capability of the CBC 10 electrode, highlighting its suitability for sensitive TMP sensing.

4.4. Effect of pH and Differential Pulse Voltammetric Determination of Trimethoprim

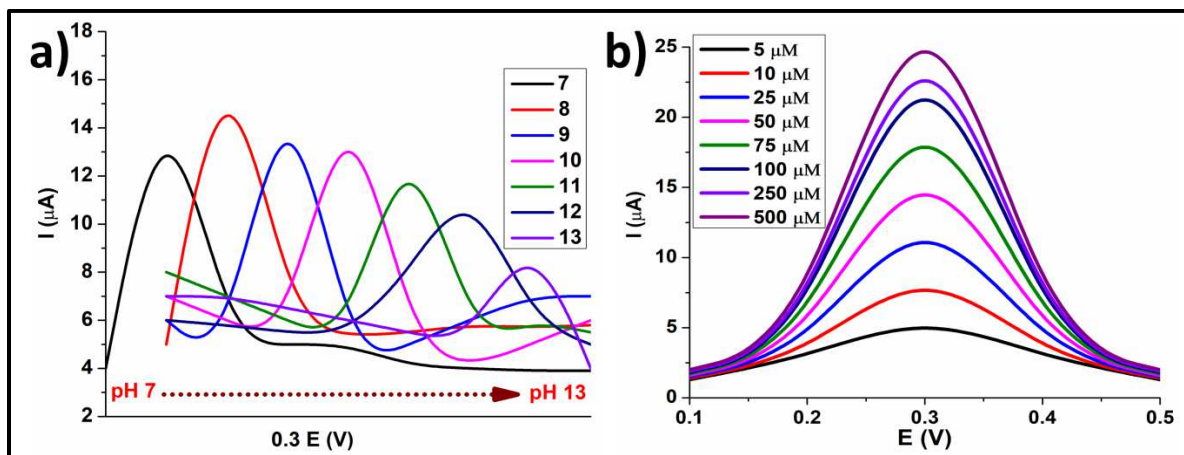


Figure 10. (a) DPV curves of 500 μM TMP at CBC 10 with different pH values from 7 to 13; (b) DPV curves of 5–500 μM TMP in 0.1 M PBS (pH 8).

Figure 10a illustrates the effect of solution pH on the differential pulse voltammetry (DPV) response of the BaCeO_3 , CBC 5, CBC 10, and CBC 20 modified electrodes toward trimethoprim (TMP) detection over the pH range of 7–13. The oxidation peak current gradually increases with increasing pH and reaches its maximum at pH 8, indicating that slightly alkaline conditions provide the most favorable environment for TMP oxidation. This enhancement is attributed to the increased availability of hydroxyl ions, which facilitates proton-coupled electron transfer and accelerates the oxidation kinetics at the electrode surface [56]. At pH values above 8, the oxidation peak current decreases slightly, which may be due to excessive adsorption of hydroxyl ions and partial blockage of the electroactive sites, thereby hindering electron transfer. In addition, the gradual shift in oxidation peak potential with increasing pH confirms the involvement of protons in the electrochemical oxidation mechanism of TMP. These results demonstrate that pH 8 is the optimum condition for achieving maximum electrocatalytic activity and sensitive electrochemical detection of TMP using the CBC-modified electrodes.

The electroanalytical performance of the BaCeO_3 , CBC 5, CBC 10, and CBC 20 modified electrodes was further evaluated by differential pulse voltammetry under the optimized experimental conditions. **Figure 10b** presents the DPV responses recorded for TMP concentrations ranging from 5 to 500 μM . The oxidation peak current increases systematically with increasing TMP concentration, indicating efficient electrocatalytic oxidation and rapid electron transfer at the electrode surface. The corresponding calibration plot exhibits an excellent linear relationship between the oxidation peak current and TMP concentration over the investigated concentration range, demonstrating the high sensitivity, wide linear detection range, and excellent quantitative sensing capability of the modified electrodes. Among the investigated samples, the CBC 10 electrode exhibited the highest current response, confirming that the optimized Ca doping level significantly enhances the electroactive surface area and charge-transfer efficiency, making it the most promising electrode for sensitive TMP detection.

The analytical capability of the fabricated electrochemical sensor was assessed by determining its limit of detection (LOD), which was found to be 0.03 μM . The sensitivity of the CBC 10

nanoparticle-modified electrode, obtained from the slope of the calibration curve, was calculated to be $0.5 \text{ mA } \mu\text{M}^{-1} \text{ cm}^{-2}$. To further validate its sensing performance, the proposed sensor was compared with previously reported electrochemical platforms for trimethoprim (TMP) determination, and the corresponding data are presented in **Table 2**. The comparison indicates that the CBC 10-based sensor delivers outstanding analytical performance, combining high sensitivity, a low detection limit, and an extensive linear response range. These characteristics demonstrate its suitability as a reliable and efficient electrochemical sensing platform for the quantitative determination of TMP.

Table 2: Comparison of CBC 10 nanoparticles with other TMP sensors based on different materials

Sl No	Electrode Material / Modifier	Linear Range (μM)	LOD (μM)	Sensitivity / Remarks $\text{mA } \mu\text{M}^{-1} \text{ cm}^{-2}$	Reference
1	(e-AgNPs) immobilized on aluminum substrates	0.01- 100	0.00384	--	[57]
2	CPE/Ag/Au NPs	0.01-120	0.003	0.42	[35]
3	ZnO/CPE	0.8 –10	0.02	--	[58]
4	CBC 10	0.05 - 100	0.03	0.5	Present work

Conclusion:

In summary, Ca-doped BaCeO₃ nanoperovskites were successfully synthesized via a sol–gel route and demonstrated excellent photocatalytic and electrochemical performance toward trimethoprim (TMP). Ca doping effectively modified the crystal structure by inducing oxygen vacancies, narrowing the optical band-gap, and promoting charge separation, thereby enhancing the overall functional properties. Under the optimized conditions (35 ppm TMP, 0.7 g catalyst, pH 7), the photocatalyst achieved a degradation efficiency of 96%. Electrochemical studies using the modified electrode exhibited a linear response over the concentration range of 0.05 – 100 μM with a low detection limit of 0.03 μM , confirming its high sensitivity for TMP determination.

The enhanced dual-functional performance highlights the effectiveness of defect engineering through Ca doping in BaCeO₃ nanoperovskites. These findings demonstrate the potential of the developed material as a promising platform for pharmaceutical pollutant remediation and electrochemical monitoring, offering new opportunities for multifunctional environmental applications.

Statements and Declarations

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Competing interests

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

Data availability statement

The data supporting the findings of this study are available within the article. Additional data related to this work are available from the corresponding author upon reasonable request.

Supplementary information

Additional characterization data, including Raman spectra and X-ray photoelectron spectroscopy (XPS) analysis of the Ca-doped BaCeO₃ nanoperovskite, are provided in the Supporting Information. The Supporting Information is available with the online version of this article.

CRedit authorship contribution statement

Goddanapura Basavegowda Yogesh: Investigation, Methodology, Writing – original draft, Writing – review & editing. Hosakere Doddarevanna Revanasiddappa: Conceptualization, Supervision, acquisition, Methodology, Visualization, Formal analysis, Writing – review & editing. Mahadev Prema: Visualization, Formal analysis, review & editing. Gowdanakatte Rameshaiah Gagana: Review & editing. Ganganagappa Nagaraju: Visualization, Formal analysis. Swamy Sreenivasa: review & editing.

Ethical approval

This article does not contain any studies involving human participants, human tissues, or animals performed by any of the authors. Therefore, ethical approval was not required for this study.

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