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Synthesis and Evaluation of Boron, Cerium, and Silver Ternary Doped Titanium Dioxide Photocatalysts for Degradation of Ciprofloxacin (CIP) Antibiotic under UV - A Irradiation

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Abstract: ***Due to the development of antimicrobial resistance, the continued presence of antibiotic residues in freshwater sources is a growing global concern and hence, it is necessary to degrade the antibiotics present in the polluted waters. In this study, three different boron, cerium, and silver ternary-doped TiO_2 photocatalysts with specific compositions were synthesized using the eco-friendly EDTA citrate method. The specific compositions investigated here are $B_1Ce_{0.1}Ag_{0.06}TiO_2$, $B_1Ce_1Ag_{0.06}TiO_2$, and $B_1Ce_1Ag_{0.1}TiO_2$. From DLS analysis, the particle size of the synthesized catalysts was found to be in the range of 125 – 500 nm. The XRD spectra confirmed the presence of cerium. The DRS analysis showed the bandgap energy of the synthesized catalysts to be in the range of 2.7 – 2.8 eV. ICP-OES analysis was done to check the leaching of the dopants from the catalysts into the solution and the results showed that silver did not leach out while boron (~0.2 ppm) and cerium (~ 0.1 ppm) were present in trace amounts. The catalysts were also evaluated for the degradation of ciprofloxacin antibiotic under UV-A light. At optimized conditions, the best performing photocatalyst namely, $B_1Ce_1Ag_{0.1}TiO_2$ showed ~54% degradation of the antibiotic in 120 min. This is attributed to the increased amounts of cerium and silver. Although the performance under UV-A irradiation is not encouraging, these results suggest that these catalysts may be more effective under visible or solar light and further work is needed to check the effectiveness under visible light irradiation as well as on larger scales of treatment.***

Keywords: Photocatalyst, Antibiotic, Ciprofloxacin, Doping, Titanium dioxide

1. Introduction

In today's world, the treatment of waste waters from pharmaceutical industries is a major issue due to the sustained presence of the antibiotic residues in the treated water samples leading to the formation of antimicrobial resistance (AMR) [1]. The consequence of AMR is that the superbugs formed due to this phenomenon will be very difficult to treat by conventional antibiotics available today and hence AMR is expected to be one of the leading causes of mortality in the next few decades. Thus, it is very essential to treat this wastewater as soon as possible to remove both the antibiotics as well as the superbugs. Photocatalysis is a capable and promising technology for the treatment of persistent or refractory substances present in wastewaters [2] and in this context, the design of multifunctional photocatalysts capable of simultaneous degradation as well as disinfection is very much required. In this work,*three* ternary doped Titanium Dioxide photocatalysts with boron cerium and silver as the dopants have been synthesized using the facile and ecofriendly EDTA citrate method [3]. These synthesized catalysts have been evaluated in the degradation of ciprofloxacin antibiotic under UV-A irradiation. The characterization of these catalysts has also been performed using a variety of tools such as SEM, DRS, BET Surface area etc.

2. Experimental Methodology

Materials

The following chemicals were used without further purification in the synthesis of the catalysts: TiO_2 (Degussa P25, 99.9% pure) from Evonik (Japan), Boric acid, EDA, citric acid and ammonia solution from Loba Chemie Pvt Ltd. (India), Cerium nitrate and silver nitrate from Sigma-Aldrich (India), Ciprofloxacin from Sigma-Aldrich (USA). Distilled water was employed in the preparation of all solutions.

Synthesis of Nanoparticles

Three ternary doped TiO_2 catalysts were made [4] using the modified sol-gel method (see Fig. 1), employing EDTA & citric acid as the chelating and complexing agents respectively. A mole ratio of 1:1:1.5 being the ratio of metal ions to EDTA and citric acid was used in the synthesis. EDTA ($C_{10}H_{16}N_2O_8$) solution was made using water and ammonia. Stoichiometric quantities of boric acid (H_3BO_3), cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$), silver nitrate ($AgNO_3$), and titanium dioxide (TiO_2) in aqueous form was added to the solution & stirred. Then, solid citric acid ($C_6H_8O_7$) was added to the above mixture. Ammonia is used for adjusting the pH to 9, and the resulting mixture was agitated gently till an organometallic gel formed. Drying of the gel was done a laboratory oven at 150 °C for 24 h. The dried sample was finely crushed and subjected to calcination in a muffle furnace at 350 °C for 12 h, followed by calcining at 600 °C for 5 h. The powder thus obtained was stored in an air-tight bottle for further use.

In this work, three doped catalysts are synthesized and denoted as 1B-0.1Ce-0.06Ag-TiO_2, 1B-1Ce-0.06Ag-TiO_2, 1B-1Ce-0.1Ag-TiO_2. Due to the use of water as a solvent thus replacing the volatile organic solvents usually employed, the process can be considered as relatively green [4]. It may be noted that Boron is an excellent disinfectant [5] and cerium promotes the adsorption capability of the

catalyst [6] while silver has excellent antimicrobial properties and surface plasmon resonance [7] enabling the catalysts functioning under visible or solar light. We wanted to examine in detail, the effect of increased amounts of cerium and silver in this work keeping the amount of boron dopant constant.

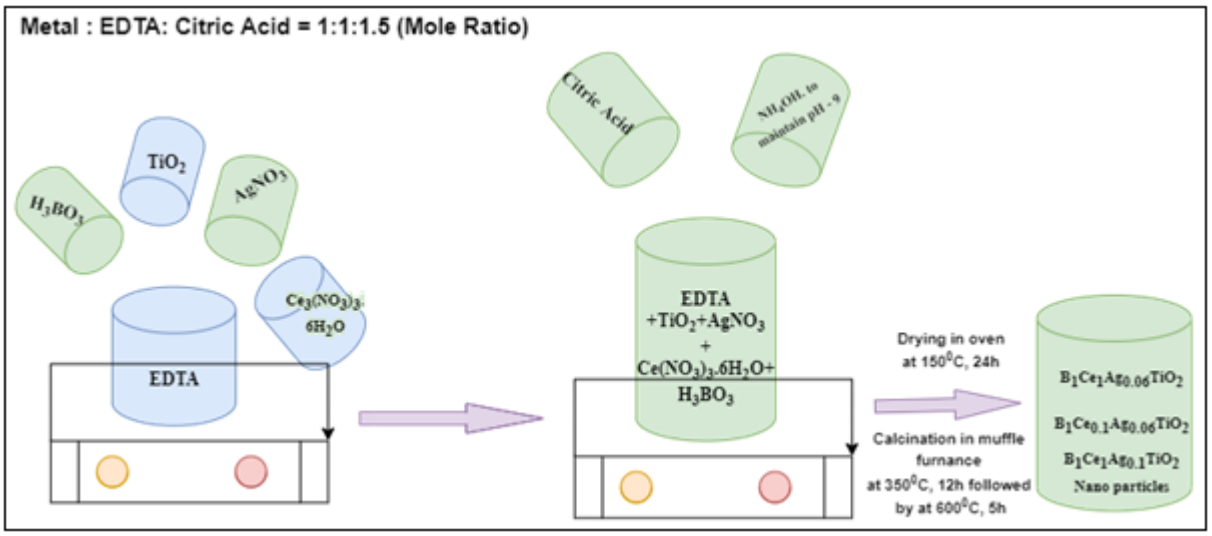


Figure 1: Schematic describing the EDTA-citrate synthesis method

Photocatalytic Degradation of Ciprofloxacin antibiotic

The photocatalytic degradation of ciprofloxacin (designated as CIP) under UV-A irradiation is used to evaluate the performance of TiO_2 and the synthesized photocatalysts. A irradiation time of 2 hours with a mean intensity of 200± 20 lx and a temperature of 27°C is used in the conduct of experiments. The volume is 200 mL of 10 mg/L, 20 mg/L, and 30 mg/L pollutant concentration (CIP) and the catalyst loading is chosen as 1 g/L. The samples are kept in the dark for 60 minutes to attain complete adsorption before starting the illumination. Liquid samples are taken at regular time intervals and filtered & centrifuged to remove the solid catalyst particles. The percentage of CIP was calculated according to the following equation:

$$\text{CIP degradation} = \frac{c_0 - c}{c_0} \times 100\% \quad (1)$$

where C_o – Initial concentration, C - Final concentration

The calibration curve of CIP was done for different concentrations of CIP solution and is shown in Fig. 2.

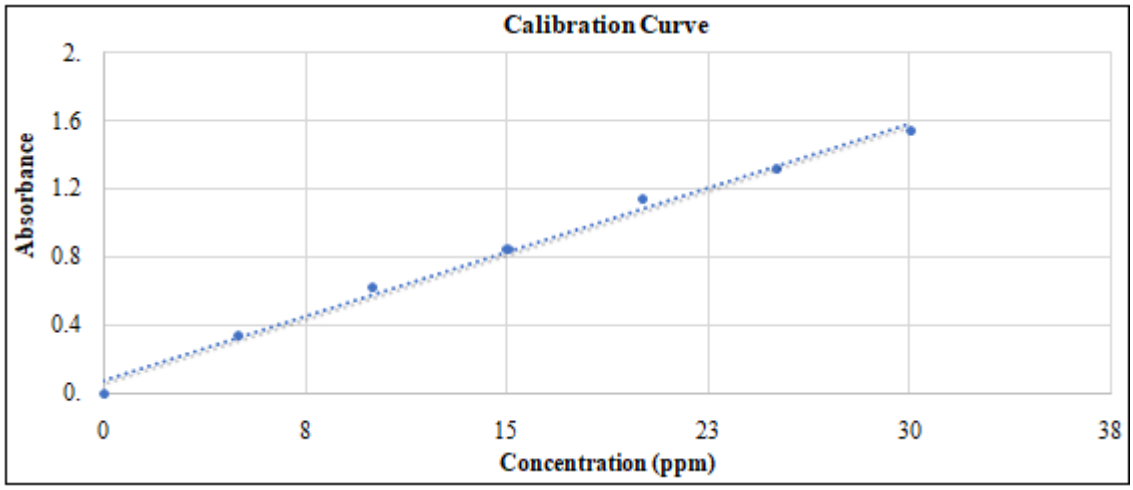


Figure 2: Calibration curve of Ciprofloxacin at λ_{max} = 287 nm

3. Results and Discussion

Particle size analysis

The particle size of the catalysts prepared was determined from the DLS analysis and the results are shown in the table below.

Table 1: Particle size of synthesized catalysts

Catalyst	Average Particle size (nm)	Band gap energy (eV)
1B-0.1Ce-0.06Ag-TiO_2	125.2	2.95
1B-1Ce-0.06Ag-TiO_2	669.9	2.96

These results seem to indicate that as the amount of dopants increases, the particle size also increases. It is possible that there is some degree of agglomeration which needs to be confirmed from SEM analysis.

BET surface area analysis

BET Surface area analysis was done for one catalyst (1B-0.1Ce-0.06Ag-TiO_2) used in this work and the specific surface area was found to be 23.3 m^2/g. This is in line with the values reported for TiO_2 based photocatalysts in the literature [8].

DRS Studies

Diffuse reflectance spectroscopy analysis was performed on the synthesized catalysts to obtain the band gap energy values as determined from the Tauc plot. In the analysis, TiO_2 is considered as an indirect semiconductor and the calculations are done on this basis. The formula used is

$$\alpha h\nu = A\left(h\nu - E_g\right)^{n/2} \quad (1)$$

where, E_g - band gap energy (eV), α - absorption coefficient, h - Planck's constant, ν - frequency of light, A - constant, n = 4 (for indirect transition). The plot of $(\alpha h\nu)^{1/2}$ versus (hν) energy determines the band gap energy values which is obtained by extrapolation of the linear portion of the curve to the x-axis. The band gap energy values determined are given in table 1 above. Relative to the band gap energy value of TiO_2 (3.2 eV), these values are slightly lower indicating that they may function well under visible or solar light irradiation.

XRD Spectra Analysis

The XRD spectra of two doped photocatalysts is shown in Fig. 3. As can be seen, the two spectra are nearly identical confirming the correctness of the synthesis procedure. The peaks observed at θ = 25.5 and 48° are indicative of the anatase phase while the small peak immediately following this at about 27° indicates the presence of the cerium oxide (111) phase. Since silver ion is relatively large compared to titanium and cerium besides being present in very low amounts, the xrd spectra do not show the presence of silver. Boron is also not indicated.

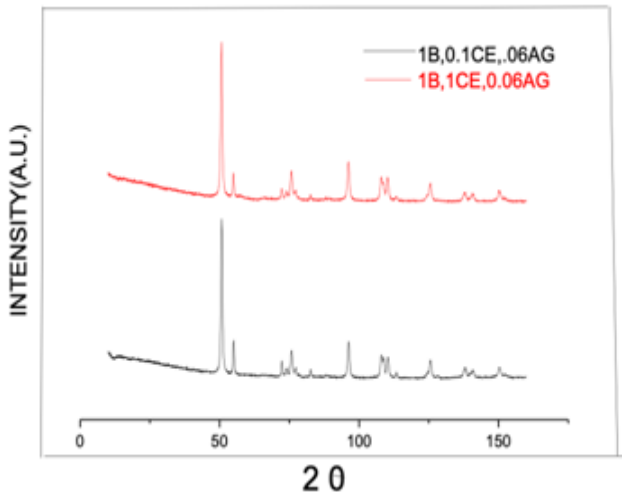
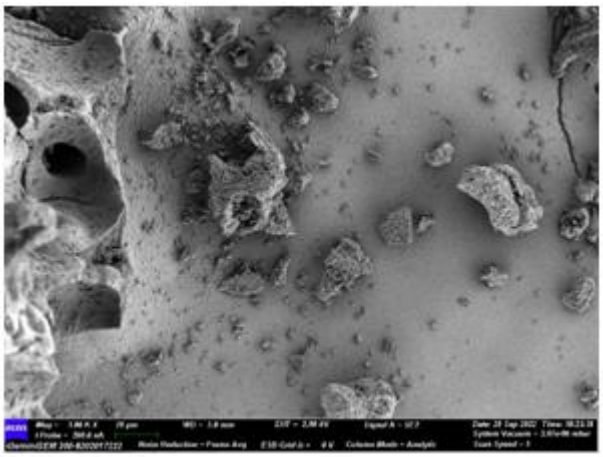


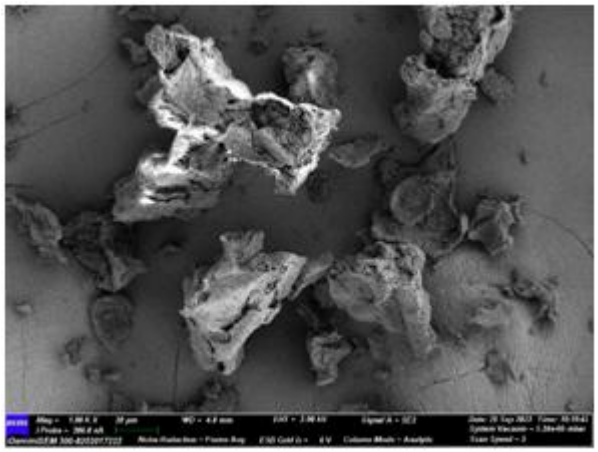
Figure 3: XRD Spectra of two doped catalysts ($B_1Ce_{0.1}Ag_{0.06}TiO_2$, $B_1Ce_1Ag_{0.06}TiO_2$).

SEM Analysis

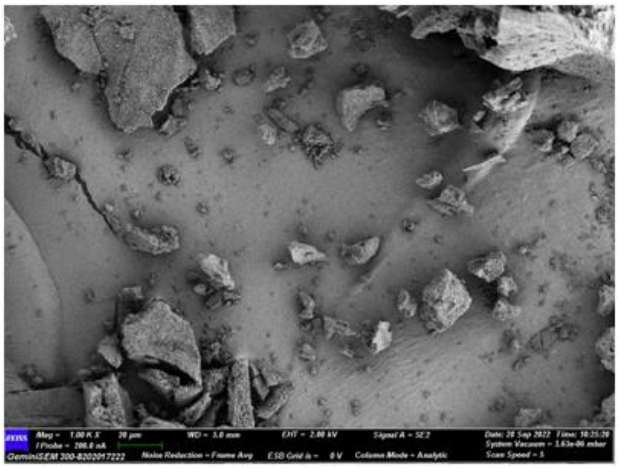
The SEM images of the three catalysts employed in this work are given in Fig. 4 below. The pictures obtained from SEM analysis show that the three catalysts are quite identical in appearance and appear as loosely packed irregular or elongated aggregates with a coarse surface.



(a) $B_1Ce_{0.1}Ag_{0.06}TiO_2$



(b) $B_1Ce_1Ag_{0.06}TiO_2$



(c) $B_1Ce_1Ag_1TiO_2$

Figure 4: SEM Images of the doped catalysts.

Photocatalytic degradation of CIP

The degradation studies of CIP for the tri-doped photocatalysts i.e., $B_1Ce_1Ag_{0.1}TiO_2$, $B_1Ce_1Ag_{0.06}TiO_2$, and$B_1Ce_{0.1}Ag_{0.06}TiO_2$ were carried out under UV-A light at room temperature for three different concentrations of CIP (Fig. 5) at a catalyst loading of 1 g/L. To compare the tri-doped catalyst performance with TiO_2, the degradation study was carried out with TiO_2. TiO_2 showed almost 100%

degradation in all the cases which is expected as this catalyst works more efficiently under UV irradiation. Also compared to TiO_2, the tridoped photocatalysts do not show significantly better adsorption. From Fig. 5, it is evident that $B_1Ce_1Ag_{0.1}TiO_2$ is the best performing catalysts across the concentrations of CIP studied giving around 54% at 10 ppm concentration.

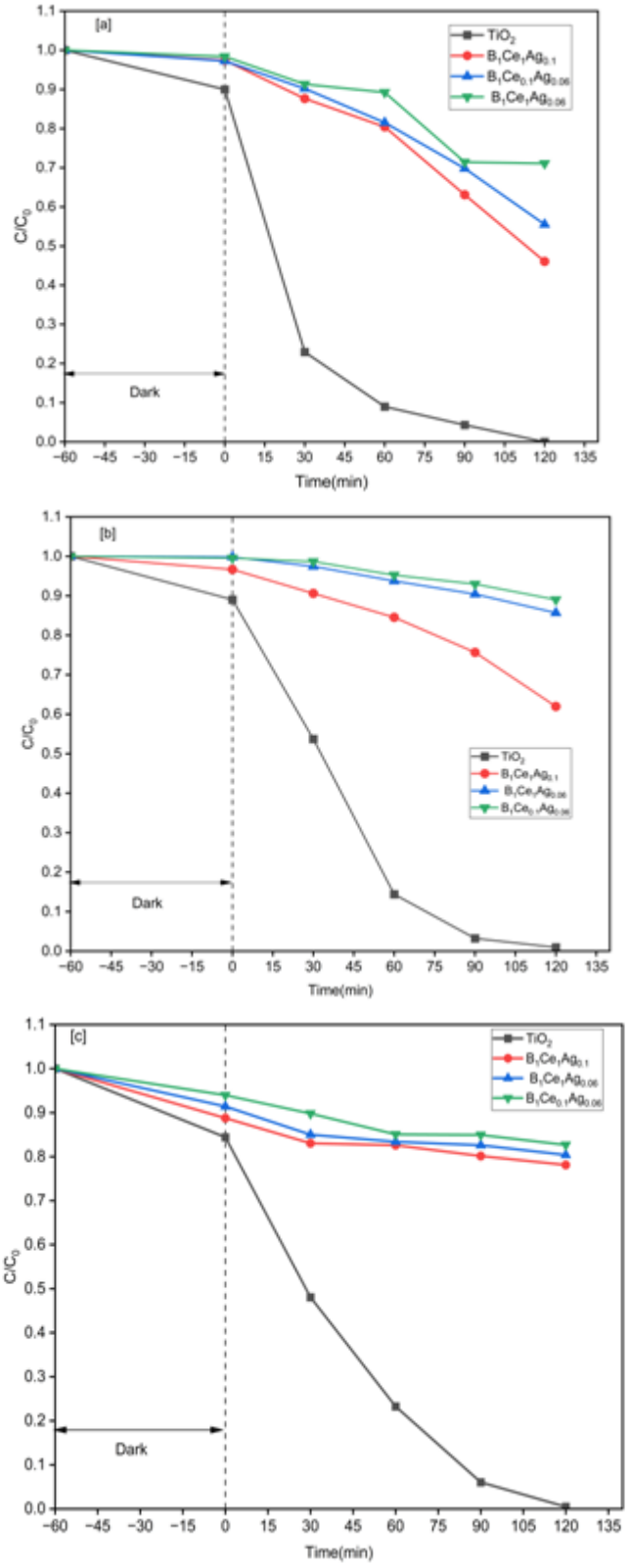


Figure 5: Effect of photocatalysts on CIP solution of (a) 10ppm (b) 20ppm (c) 30ppm concentration

4. Conclusions

In this study, the photocatalyst degradation of ciprofloxacin antibiotic has been carried out by using three tri-doped photocatalysts i.e., $B_1Ce_1Ag_{0.1}TiO_2$, $B_1Ce_{0.1}Ag_{0.06}TiO_2$, and $B_1Ce_1Ag_{0.06}TiO_2$. The photocatalytic degradation capability of $B_1Ce_1Ag_{0.1}$was comparatively higher than the remaining two doped catalysts, as it degraded 54% in 120 min. These results concluded that $B_1Ce_1Ag_{0.1}TiO_2$ was the best performing tri-doped photocatalyst. The performance of the tri-doped catalysts under UV-A irradiation was not encouraging and these catalysts need to be tested under visible or sun light for obtaining better results. Further work is needed to check the effectiveness of the catalyst in large scale.

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