



A Study of BiVO₄ and CeO₂ Composite Photocatalytic Materials for the Removal of Tetracycline Hydrochloride from Water

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Abstract. Tetracycline hydrochloride (TC) is a tetracycline antibiotic characterized by a complex structure, prolonged persistence, and widespread environmental contamination. To address this, BiVO₄ and CeO₂ composite photocatalysts (BVC) were synthesized via high-temperature hydrothermal method for the degradation of TC under visible light irradiation. The study examined the impact of various BiVO₄/CeO₂ ratios on the photocatalytic performance of the composite. Results indicated that the composite photocatalyst (BVC) significantly outperformed individual BiVO₄ and CeO₂ in degrading TC, with the highest degradation rate and photocatalytic efficiency observed for the BVC composite with a 1:1 mass ratio of BiVO₄ to CeO₂.

Keywords: photocatalysis, TC, BiVO₄/CeO₂.

1 Introduction

Water environment pollution not only restricts the sustainable development of society and economy [1], but also poses a potential threat to human health and ecological safety, making it essential to develop efficient and eco-friendly water treatment technologies [2]. Among pollutants, tetracycline hydrochloride (TC), a tetracycline antibiotic with a complex structure, prolonged persistence [3], wide contamination range, and propensity to promote antibiotic resistance genes, has frequently been detected in aquatic environments. Photocatalytic semiconductors, as advanced oxidation technologies powered by light energy, hold significant promise for environmental pollution control and have become a focal point of research in environmental science. Although bismuth vanadate (BiVO₄) and cerium oxide (CeO₂) exhibit fundamental photocatalytic capabilities, both materials are hindered by high photogenerated carrier recombination rates and low visible-light responsiveness [4, 5]. This study focuses on a BiVO₄/CeO₂ composite system aimed at improving photocatalytic degradation of TC. By systematically examining the effects of various BiVO₄/CeO₂ ratios on the photocatalytic degradation of TC, this work identifies compositions with enhanced degradation efficiency, offering valuable insights for the development of more efficient environmental purification technologies.

2 Experimental section

2.1 Preparation of photocatalysts

BiVO₄: 2 mmol of Bi(NO₃)₃·5H₂O and NH₄VO₃ were weighed and dissolved in 30 mL of deionized water, followed by the addition of 3.12 g of NaHCO₃. The mixture was stirred for 40 minutes, then transferred to a reactor and heated to 120 °C for 2 hours. The resulting product was filtered and dried to obtain a pale yellow BiVO₄ powder.

CeO₂: 1 mmol/L Ce(NO₃)₃·6H₂O was dissolved in 35 mL of 9 mol/L NaOH solution and stirred for 2 hours. The solution was then transferred to a reactor and heated at 100 °C for 24 hours. After filtration and drying, a white precipitate was obtained. This precipitate was calcined in a muffle furnace at 500 °C for 4 hours, producing yellow CeO₂ nanorods.

BVC: BiVO₄ and CeO₂ precursors were combined in molar ratios of 1:5, 1:3, 1:1, 3:1, and 5:1 to obtain the BiVO₄/CeO₂ composite photocatalyst (BVC).

2.2 Characterization of photocatalysts

X-ray diffraction (XRD) was employed to analyze the lattice structure and chemical composition of the materials, using a copper target with a scanning range of 5° to 90° and a scanning speed of 10°/min. The surface morphology and structure of the samples were examined through scanning electron microscopy (SEM). Electrochemical properties, including impedance and photocurrent responses, were measured using a CHI760E electrochemical workstation.

2.3 Photocatalytic activity testing

A 50 mL TC solution with a concentration of 30 mg/L was measured into a beaker, and 20 mg of photocatalyst was added to the solution. The mixture was stirred using a multi-head magnetic stirrer, with a short-arc xenon lamp serving as the light source. Prior to the photocatalytic reaction, the solution containing the catalyst was maintained in a dark environment with stirring for 40 minutes to ensure equilibrium between adsorption and desorption in the reaction system. After this dark reaction phase, a 3 mL sample was extracted using a syringe, filtered through a membrane, and collected in a 5 mL centrifuge tube. The system was then exposed to visible light with continuous stirring, and samples were collected every 10 minutes over a total light exposure time of 60 minutes, following the same sampling procedure. The eight collected samples were analyzed using a UV-Vis spectrophotometer, and the residual concentration of TC was calculated from the absorbance of each sample using Lambert's law. The degradation rate of TC by different photocatalysts at different time intervals was thus determined from the residual concentration data.

3 Results and discussion

The crystal structure and phase structure characteristics of the material were characterized by XRD. As shown in Fig. 1a, the prepared bismuth vanadate monomer is in basic agreement with the standard XRD (PDF#00-014-0688) card of the corresponding BiVO₄, indicating the high purity of the synthesized sample. The cerium oxide monomer basically matches the standard XRD (PDF#04-005-9598) card of the corresponding CeO₂, indicating the high purity of the synthesized samples. The XRD plots of the composite photocatalyst (BVC) where 2θ values at 15.141°, 28.947°, 30.548°, 34.494°, and 35.222° correspond to the (020), (121), (040), (200), and (002) faces of BiVO₄, respectively [6]. The 2θ values at 28.609°, 33.153°, 47.590°, and 56.472° corresponding to the (111), (200), (220), and (311) facets of CeO₂

[7], respectively, indicating the successful composite of BiVO_4 with CeO_2 .

The prepared BiVO_4 monomers exhibited an irregular particle form, as shown in Fig. 1b. The synthesized CeO_2 monomer displayed a block structure with stacked nanorods, as depicted in Fig. 1c. Upon hydrothermal mixing of bismuth vanadate with cerium oxide nanorods to form a composite photocatalyst (Fig. 1d), the CeO_2 nanorod structure remained intact, while numerous small spherical BiVO_4 particles attached to the surface. This observation confirms the successful compositing of BiVO_4 with CeO_2 [8].

As shown in Fig. 2a, CeO_2 exhibited the weakest photocatalytic degradation performance for tetracycline (TC), with a degradation rate of less than 40% within 60 minutes of photodegradation. For different $\text{BiVO}_4/\text{CeO}_2$ ratios in the composite photocatalysts (BVC), the TC degradation rate increased as the BiVO_4 content decreased from a 1:5 to 1:3 and subsequently to a 1:1 ratio, indicating enhanced photocatalytic activity. However, as the CeO_2 content increased from 1:1 to 1:3 and further to 1:5, the TC degradation efficiency gradually declined. Among all tested ratios, the BVC composite catalyst with a 1:1 ratio exhibited the highest TC degradation rate, reaching 90% after 60 minutes of photodegradation. According to Fig. 2b, it can be seen that the reaction rate constant of BVC (1:1) is 0.03774 min^{-1} , which is significantly higher than that of the monomer and is 5.5159 and 15.0418 times higher than that of the monomers BiVO_4 and CeO_2 , respectively. Meanwhile, we tested the stability of the catalyst, as shown in Fig. 2c, the degradation rate of BVC (1:1) catalyst on TC could still be maintained above 50% after four times of reuse, which indicated its good cycling performance. Tab 1 provides a comparison with previous studies on the catalytic degradation of tetracycline hydrochloride.

In Fig. 2d, the photocurrent of the composite photocatalyst (BVC) was significantly higher than that of the BiVO_4 and CeO_2 monomers, with an instantaneous photocurrent density reaching up to $0.55 \mu\text{A}$, indicating the highest separation efficiency for photogenerated electrons (e^-) and holes (h^+). Fig. 2e shows the electrochemical impedance spectra (EIS) of the samples, with the Nyquist semicircle diameter reflecting the magnitude of charge transfer resistance [5]. The charge transfer resistance has a substantial effect on the separation efficiency of photogenerated carriers. As seen in the figure, the Nyquist radius order was $\text{CeO}_2 > \text{BiVO}_4 > \text{composite photocatalyst (BVC)}$, demonstrating that the BVC composite photocatalyst had the lowest photogenerated carrier transfer resistance, the highest carrier separation efficiency, and the highest photocatalytic activity among the samples.

The free radical trapping experiments allowed an in-depth analysis of the intrinsic mechanism of the photocatalytic degradation process and precise identification of the main reactive species with EDTA, p-isopropanol (IPA) and 2,2,6,6-tetramethylpiperidinium oxide (TEMPO) as h^+ , $-OH$, and $-O_2^-$, respectively [9]. As shown in Fig. 2f, the degradation rate of TC by the 1:1 ratio composite photocatalyst (BVC) did not decrease significantly when IPA and Tempo were added to the system, and the degradation rate was about 75%; the degradation rate decreased from 92% to 16% when EDTA was added, which is a decrease of about 76%. The experimental results showed that the hole (h^+) played a key role in the photocatalytic degradation system of TC with the ratio of BVC of 1:1.

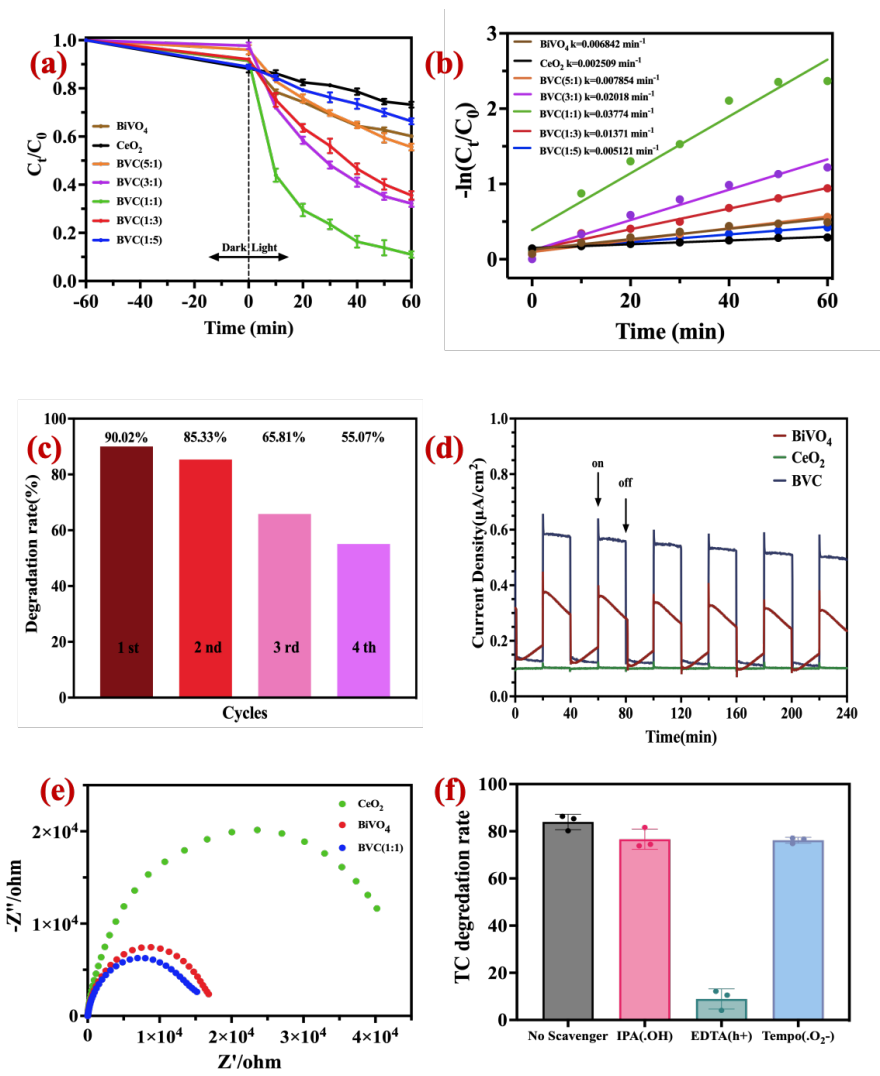


Fig. 2. (a) photodegradation performance of different photocatalyst samples (20 mg) on TC (50 mL, 30 mg/L) under UV-visible irradiation; (b) first-order kinetic model fitting for photocatalytic degradation of 50 ml of 30 mg/L TC with different catalysts; (c) BVC (1:1) photocatalytic cycle test; (d) photocurrent response plots of BiVO₄, CeO₂ and BVC (1:1); (e) electrical impedance spectra of BiVO₄, CeO₂ and BVC (1:1); and (f) the radical trapping experimental results. All the above experiments were done at about 25 °C.

Tab 1. Photocatalytic degradation of TC by TiO₂, g-C₃N₄ and ZnO

Photocatalyst	Light	TC	Catalyst dosage	Degradation rate	Reference
bulk g-C ₃ N ₄	300 W XL	10 mg/L	5 mg	40% (120 min)	[10]

g-C ₃ N ₄	5 W LED	30 mg/L	50 mg	47% (60 min)	[11]
amorphous nanosheet g-C ₃ N ₄	500 W XL	10 mg/L	50 mg	48.7% (150 min)	[12]
ZnO	LED	40 mg/L	30 mg	37.42% (120 min)	[13]
hollow ZnO microspheres	visible-light	20 mg/L	15 mg	63.09% (90 min)	[14]
ZnO particles	300 W XL	1g/L	60 mg	cannot undergo self-degradation (60 min)	[15]
TiO ₂	LED	40 mg/L	30 mg	70.36% (120 min)	[13]
TiO ₂ microspheres	300 W XL	20 mg/L	50 mg	78% (60 min)	[16]
TiO ₂ particles	LED	20 mg/L	25 mg	55.3% (120 min)	[17]

4 Conclusion

The effects of BiVO₄ and CeO₂ contents in molar ratios of 1:5, 1:3, 1:1, 3:1, and 5:1 on the photocatalytic performance of the composite photocatalysts (BVC) were evaluated. The composite catalyst with a 1:1 molar ratio exhibited the highest photocatalytic activity, attributed to enhanced photogenerated carrier separation efficiency and a substantial reduction in recombination rate. This decrease in recombination rate effectively suppressed the recombination of photogenerated electrons and holes during the photocatalytic reaction. Additionally, the photocatalytic activity was markedly increased, indicating the catalyst's capacity for more efficient photocatalytic degradation under light irradiation. Detailed radical trapping experiments identified that various reactive species contributed to the photocatalytic degradation process, with the hole (h⁺) identified as the key reactive species.

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Disclosure of Interests. Specifically state that the authors have no competing interests.

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