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Study on the Performance of BiOCl Photocatalyst for Degradation of Tetracycline Hydrochloride

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Abstract

Tetracycline hydrochloride (TC-HCl) is widely used in the prevention and treatment of human/animal bacterial infection due to its good antibacterial activity. However, because of its high hydrophilicity and low volatility, TC-HCl can enter the natural water body through various ways and exist in it statically for a long time, which then causes environmental toxicity and even threatens human health. Photocatalysis, which can use free, clean and sustainable solar energy to provide power, achieves the conversion of solar energy to chemical energy and is a promising green technology for solving global environmental and energy challenges. BiOCl has suitable valence/conduction potential and good stability and hierarchical structure, which contributes to smooth transfer of surface charge. BiOCl photocatalyst materials with deionized water, anhydrous ethanol (EtOH), and ethylene glycol (EG) as solvents were prepared by using different viscosity solutions as reaction media. The characterization results showed that the type of solvent is what mainly affected the morphology and absorption intensity of the photocatalyst. BiOCl prepared with EG as solvent has the best photocatalytic degradation performance of TC-HCl, and the removal rate can reach 76% after 60 min of visible light irradiation. Its strong light response intensity and unique spherical structure contribute to the enhancement of photocatalytic activity.

Keywords: BiOX; BiOCl; antibiotics; tetracycline hydrochloride; photocatalytic



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1. Introduction

With the rapid development of modern industry, substantial amounts of organic pollutants have entered aquatic environments, leading to increasingly severe water pollution. Antibiotics, in particular, have emerged as a major class of contaminants due to their widespread use and persistence. Tetracycline hydrochloride (TC-HCl) is one of the most commonly used antibiotics worldwide for human therapy and animal husbandry due to its broad-spectrum efficacy and low cost. However, because of its high hydrophilicity and low biodegradability, a significant portion of TC-HCl is excreted unchanged, allowing it to enter aquatic ecosystems through various pathways. Its persistent presence in water bodies can promote the development of antibiotic-resistant genes and bacteria, posing a significant threat to ecosystem balance and human health [1,2]. Consequently, researchers have extensively explored effective treatment methods to eliminate TC-HCl from water bodies. Among various advanced oxidation processes (AOPs), semiconductor-based photocatalysis

has been demonstrated as a promising green technology [3] for the degradation of organic pollutants like TC-HCl, as it utilizes sustainable solar energy to drive the degradation process. While titanium dioxide (TiO_2) is one of the most widely studied photocatalysts, its large bandgap (~ 3.2 eV) restricts its activity to the ultraviolet region of solar light, which constitutes only a small fraction ($\sim 5\%$) of the solar spectrum. This limitation has spurred the search for alternative photocatalysts with better visible light responsiveness [4]. BiOCl—comprising $[\text{Bi}_2\text{O}_2]^{2+}$ slabs interleaved with double Cl^- layers—has garnered significant attention as one of the most valuable photocatalytic materials for pollutant degradation [4,5]. This prominence arises from its advantageous properties: exceptional chemical/optical stability, environmental compatibility, and low cost. Its unique layered structure endows it with an internal static electric field, which is highly beneficial for the effective separation of photogenerated electron–hole pairs [6,7]. Previous studies confirm that its suitable band structure and unique layered architecture enable efficient organic pollutant degradation [6,7]. Crucially, the morphology and dimensions of BiOCl materials are pivotal factors in enhancing both adsorption capacity and photocatalytic activity.

The photocatalytic performance of a semiconductor is intrinsically governed by three fundamental processes: light absorption, charge carrier separation and migration, and surface reaction efficiency. A current major trend in the field involves tailoring the morphology and dimensions of photocatalysts to enhance all these aspects simultaneously [8]. For BiOCl materials, these characteristics are pivotal factors in enhancing both adsorption capacity and photocatalytic activity.

During material synthesis, solvent viscosity is a critical parameter that governs ion diffusion rates and modulates crystal growth kinetics, thereby directly influencing the final morphology. The viscosity of the solvent medium can significantly affect the nucleation process and the subsequent oriented attachment and self-assembly of nanocrystals [9,10]. Given BiOCl's characteristic layered structure, appropriate solvents can not only facilitate the formation of thinner nanosheets but also act as structure-directing agents to induce nanosheet self-assembly. This process drives the transition from two-dimensional sheet-like structures to three-dimensional hierarchical microspheres, which often exhibit superior photocatalytic performance due to enhanced light scattering, higher surface area, and improved mass transfer [8–10]. While the synthesis of BiOCl using different solvents has been reported, a systematic study directly correlating solvent viscosity to the evolution of its structural, optical, and electrochemical properties, and ultimately providing a comprehensive mechanistic explanation for the enhanced performance, is still needed.

Therefore, the novelty of this study lies in the systematic and comparative investigation of how solvents with progressively increasing viscosity—deionized water (DI), anhydrous ethanol (EtOH), and ethylene glycol (EG)—precisely tune the morphology of BiOCl and how these morphological changes concurrently alter its optical absorption, charge separation efficiency, and ultimately affect its photocatalytic activity towards TC-HCl degradation. This approach moves beyond mere morphology control and establishes a clear structure–property–performance relationship.

In this study, three solvents with progressively increasing viscosity—deionized water (DI), anhydrous ethanol (EtOH), and ethylene glycol (EG)—were employed to synthesize DI-BiOCl, EtOH-BiOCl, and EG-BiOCl photocatalysts. Their structural composition, morphological characteristics, and optoelectronic properties were systematically analyzed via X-ray diffraction (XRD), Fourier-transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), UV-vis DRS, and electrochemical impedance spectroscopy (EIS). Preliminary investigations into their fundamental properties and photocatalytic performance were conducted using TC-HCl as the target pollutant.

2. Materials and Methods

2.1. Materials

All aqueous solutions in this study were prepared with ultrapure water. Unless otherwise specified, all chemicals were of analytical grade. Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, CAS No.: 10035-06-0) and potassium chloride (KCl, CAS No.: 7447-40-7) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethylene glycol (EG, CAS No.: 107-21-1) and tetracycline hydrochloride (TC-HCl, CAS No.: 64-75-5) were obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China).

2.2. Preparation of BiOCl

2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 2 mmol of KCl were added to 60 mL EG. The mixture was stirred for 2 h until complete dissolution. Subsequently, the solution in the beaker was transferred to a 100 mL autoclave with a polytetrafluoroethylene lining and subjected to solvothermal reaction at 180 °C for 2 h in an oven. The resulting products were collected by vacuum filtration, repeatedly washed with DI and EtOH, and dried at 80 °C to obtain the EG-BiOCl photocatalyst. DI-BiOCl (using DI as solvent) and ETH-BiOCl (using EtOH as solvent) were synthesized following the identical procedure.

The synthesis protocol was highly reproducible, consistently yielding materials with identical phase purity and similar morphology across multiple batches when the stated experimental parameters (precursor concentration, solvent volume, reaction temperature, and time) were meticulously followed.

2.3. Characterization

X-ray diffraction (XRD) patterns (Cu target, $\text{K}\alpha$ radiation source; 5°/min, $2\theta = 5\text{--}80^\circ$) were obtained using a Smart Lab SE (Rigaku, Japan) diffractometer. Data refinement was performed with JADE 6 software. Scanning electron microscopy (SEM) images were obtained using a field-emission SEM (TESCAN MIRA3 LMH, Brno, Czech Republic). Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet iN10 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Elemental composition and valence states were analyzed by X-ray photoelectron spectroscopy (XPS) using an AXIS SUPRA+ spectrometer (Shimadzu, Kyoto, Japan) with Al $\text{K}\alpha$ excitation. UV-vis diffuse reflectance spectra (BaSO_4 substrate, scan range: 200–800 nm) were obtained using a UV-vis spectrophotometer (3600 Plus, Shimadzu, Japan). Electrochemical impedance spectroscopy (EIS) was conducted on a CHI 660E electrochemical workstation (Shanghai Chenhua Scientific Instrument Co., Ltd., Shanghai, China) with a standard three-electrode system.

2.4. Photocatalytic Performance Evaluation

A 300 W xenon lamp (PLS-SXE300D, PerfectLight, Beijing, China) equipped with a filter (UVCUT420, PerfectLight, Beijing, China) was used as visible light source, which was placed 12 cm away from the liquid surface of the solution. The photocatalytic activity of the catalysts was investigated using TC-HCl as the target pollutant. A schematic diagram of the photocatalytic experimental setup is illustrated in Figure 1. Typically, 100 mg of photocatalyst was dispersed in 200 mL of TC-HCl aqueous solution (30 mg/L) in a double-walled cylindrical quartz reactor. The pH of the initial TC-HCl solution was measured to be 4.2 ± 0.1 using a digital pH meter (PHSJ-4F, INESA Scientific Instrument Co., Ltd., Shanghai, China), and no further adjustment was made to investigate the photocatalytic performance under natural acidic conditions, which is common for tetracycline antibiotics solutions. The suspension was continuously stirred using a magnetic stirrer to keep the catalyst in suspension. To maintain a constant temperature of 25 ± 1 °C throughout the experiment, cooling water was circulated through the jacket of the reactor. First, the

photocatalyst sample was stirred in a dark reaction vessel for 45 min to achieve adsorption–desorption equilibrium; then, the jacketed beaker was placed under a visible light source for the photocatalytic reaction. During the latter, 3 mL of the suspension was collected every 15 min and passed through a 0.22 µm filter membrane. Subsequently, the residual concentration of TC-HCl was determined by measuring absorbance at 357 nm using a UV-vis spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan). The TC-HCl removal efficiency in the reaction system was determined using Equation (1):

$$\eta = (1 - C_t/C_0) \times 100\% \quad (1)$$

where C_t is the concentration of TC-HCl after t minutes of reaction and C_0 is the concentration of TC-HCl at the start of the reaction.

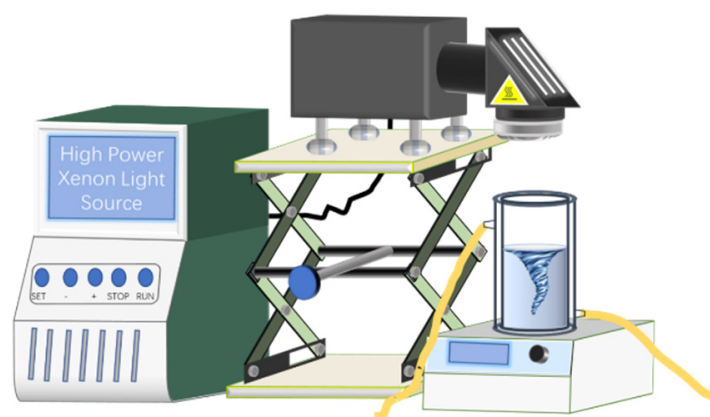


Figure 1. Schematic diagram of the photocatalytic reaction setup.

The quasi-first-order kinetic model in Equation (2) was used to fit and analyze the photocatalytic degradation data:

$$\ln(C_t/C_0) = -kt \quad (2)$$

where k is the rate constant (min^{-1}) and t is the reaction time (min).

3. Results and Discussion

3.1. Crystal Structure, Phase Composition, and Microstructure

The crystal structure and phase composition of DI-BiOCl, EtOH-BiOCl, and EG-BiOCl were analyzed by XRD. As shown in Figure 2a, the diffraction peaks at $2\theta = 12.0^\circ$, 25.9° , 32.5° , 33.5° , 40.9° , 46.7° , 49.7° , 54.1° , 58.6° , and 68.25° corresponded to the (001), (002), (101), (110), (102), (003), (112), (200), (113), (211), (104), and (212) crystal planes (ICDD No. 06-0249), confirming successful synthesis. The sharp diffraction peaks indicate high crystallinity. To quantitatively compare the crystallite sizes, the Scherrer equation ($D = K\lambda/(\beta\cos\theta)$, where D is the crystallite size, $K = 0.94$, $\lambda = 0.15406$ nm, β is the full width at half maximum (FWHM), and θ is the Bragg angle) was applied to the main (101) diffraction peak. The calculated average crystallite sizes were approximately 45.2 nm for DI-BiOCl, 32.8 nm for EtOH-BiOCl, and 28.1 nm for EG-BiOCl. This quantitative trend—where crystallite size decreases with increasing solvent viscosity—fully corroborates the qualitative morphological order observed in the SEM images (Figure 3). Broader peaks and lower intensity in the XRD patterns are indicative of smaller crystallite sizes, which is validated by the calculated values.

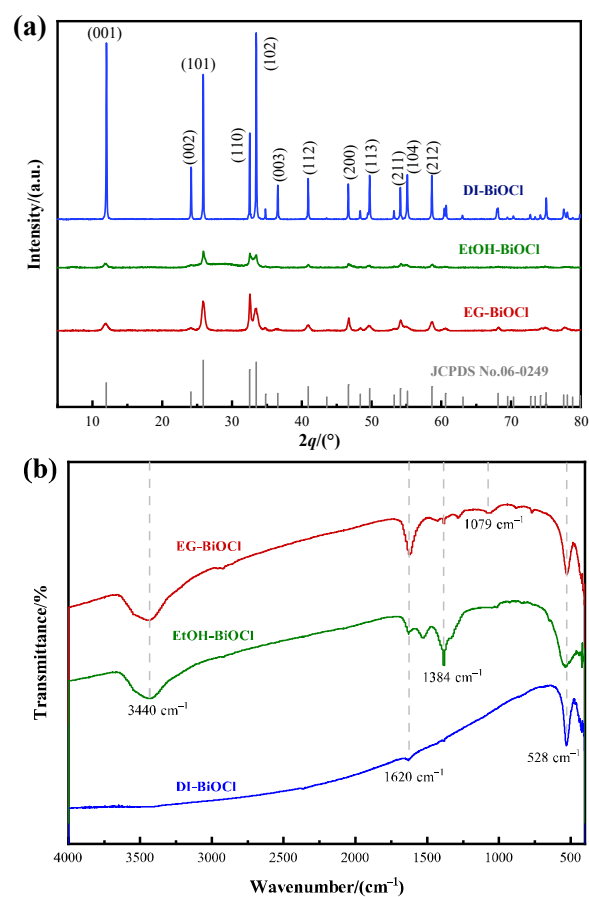


Figure 2. XRD patterns (a) and FT-IR patterns (b) of DI-BiOCl, EtOH-BiOCl and EG-BiOCl.

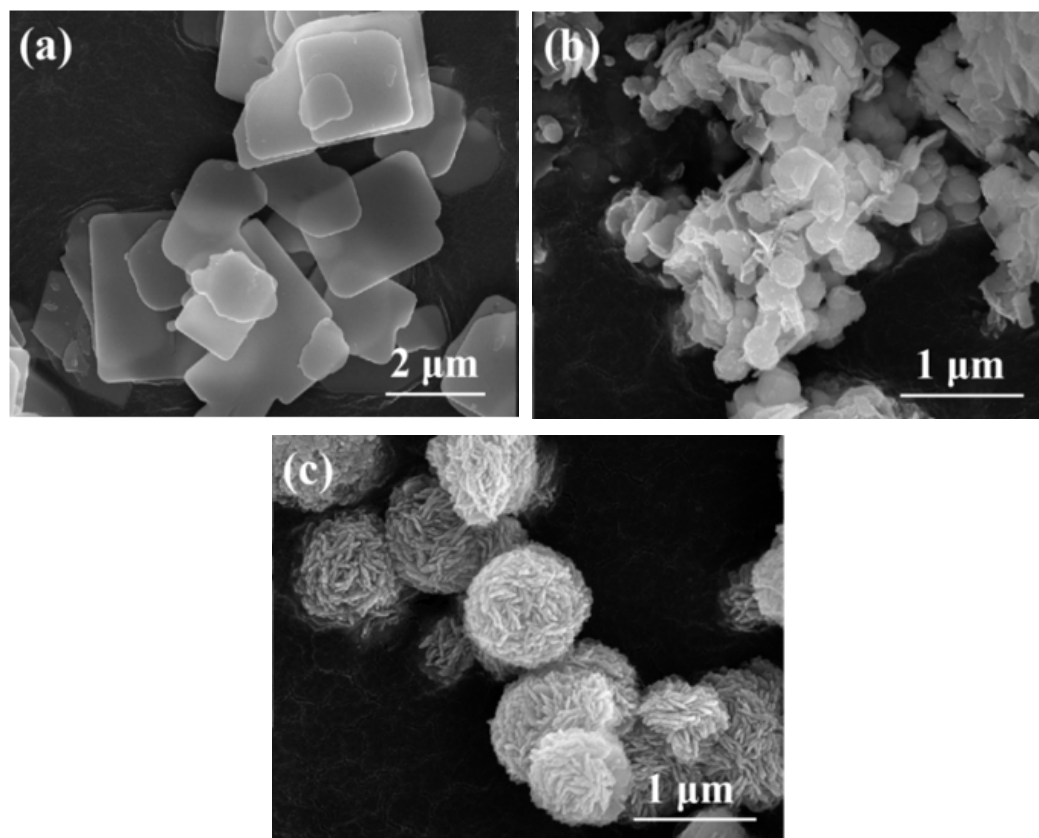


Figure 3. SEM images of DI-BiOCl (a), EtOH-BiOCl (b), and EG-BiOCl (c).

While the (102) plane dominates in DI-BiOCl, both EtOH-BiOCl and EG-BiOCl exhibit (110) as the primary plane. Notably, EtOH-BiOCl shows the weakest diffraction intensity and minimal intensity difference between primary and secondary planes. During BiOCl synthesis with EG solvent, Bi^{3+} coordinates with dihydroxyl groups of EG to form alkoxy complexes and H^+ [8,11]. This process suppresses preferential growth along the (102) direction, resulting in dominant diffraction peaks for the (110) plane.

FT-IR analysis further elucidated sample composition, with spectra displayed in Figure 2b. The absorption peak at 528 cm^{-1} corresponds to asymmetric stretching vibrations of Bi–O bonds [12]. Peaks at 1384 cm^{-1} and 1079 cm^{-1} are attributed to stretching vibrations of Bi–Cl bonds [12,13]. Absorption features at 3440 cm^{-1} and 1620 cm^{-1} arise from stretching vibrations of surface hydroxyl groups and adsorbed water molecules [14,15]. These results confirm successful synthesis of all BiOCl materials.

The morphology and structure of DI-BiOCl, EtOH-BiOCl, and EG-BiOCl were analyzed by SEM. The morphology of BiOCl varied significantly with solvent type. DI-BiOCl synthesized in deionized water (Figure 3a) exhibited sheet-like structures with lateral sizes of 1–4 μm . EtOH-BiOCl prepared in anhydrous ethanol (Figure 3b) showed irregular nanosheets similar to DI-BiOCl but with reduced dimensions (240–360 nm) and thicknesses < 100 nm, displaying partial irregular stacking.

Notably, EG-BiOCl (Figure 3c) formed distinctive spherical architectures (diameter $\sim 0.8\text{--}1\text{ }\mu\text{m}$) composed of closely stacked nanosheets (<100 nm thick). This unique configuration potentially enhances photocatalytic performance. Microsphere architectures enhance photocatalytic efficiency by providing superior light harvesting, shorter diffusion paths, faster interfacial charge separation, and increased reactive sites, as evidenced by previous studies [16,17].

3.2. Elemental Composition and Valence State Analysis

XPS characterization was performed to analyze elemental composition and chemical states of DI-BiOCl, EtOH-BiOCl, and EG-BiOCl samples, as shown in Figure 4, with all spectra calibrated using the C1s peak at 284.8 eV.

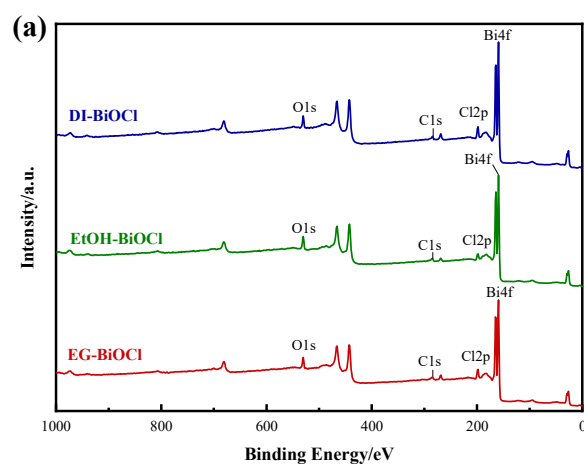


Figure 4. Cont.

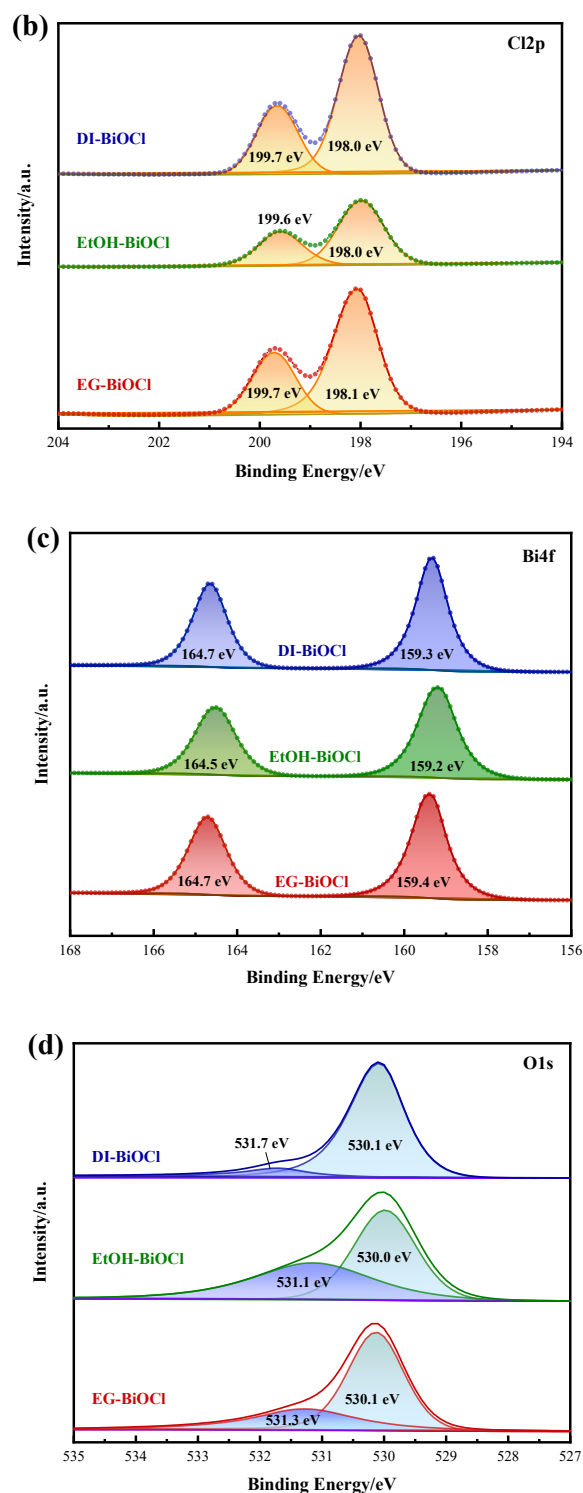


Figure 4. XPS of DI-BiOCl, EtOH-BiOCl and EG-BiOCl: (a) Full spectrum; (b) Cl2p; (c) Bi4f; (d) O1s.

As shown in the survey spectra (Figure 4a), all photocatalysts contained C, Bi, O, and Cl elements. The C1s signal originated from the instrument itself. Figure 4b,c display high-resolution spectra of Cl2p, Bi4f, and O1s. Well-defined Bi4f spin–orbit doublets with splitting energies of 5.3–5.4 eV (Figure 4c) indicate the exclusive presence of Bi³⁺ species [17,18]. All samples exhibited characteristic peaks of Bi³⁺ between 164.5 and 164.7 eV (Bi4f_{5/2}) and 159.2–159.4 eV (Bi4f_{7/2}) [19]. In Figure 4d, peaks at 530.1 eV (DI-BiOCl), 530.0 eV (EtOH-BiOCl), and 530.1 eV (EG-BiOCl) are assigned to lattice oxygen in [Bi₂O₂]²⁺ slabs. Signals at 531.7 eV, 531.1 eV, and 531.3 eV correspond to chemisorbed

oxygen species in each sample [12,20]. Additionally, high-resolution Cl2p spectra of all samples are presented in Figure 4b. Characteristic peaks for Cl2p_{3/2} and Cl2p_{1/2} orbitals in DI-BiOCl, EtOH-BiOCl, and EG-BiOCl were located at 198.0–198.1 eV and 199.6–199.7 eV, respectively, corresponding to Cl[−] species [12,14].

3.3. Optical Absorption Properties and Band Gap Analysis

UV-vis DRS analysis determined the light-harvesting capacity and spectral response range of each catalyst. As shown in Figure 5a, DI-BiOCl, EtOH-BiOCl, and EG-BiOCl exhibited no visible light response, with absorption peaks exclusively in the UV region. This confirms minimal solvent influence on the optical response range of BiOCl. However, EtOH-BiOCl showed slight redshift while EG-BiOCl displayed blueshift at the absorption edge compared to DI-BiOCl. These shifts result from EtOH-BiOCl's reduced nanosheet stacking and EG-BiOCl's microsphere architecture composed of smaller nanosheets [8]. Consequently, EtOH-BiOCl and EG-BiOCl exhibited slightly reduced and increased E_g values, respectively (Figure 5b), though all samples maintained E_g values consistent with the reported 3.4 eV [21]. Notably, EG-BiOCl demonstrated the strongest light absorption intensity, followed by EtOH-BiOCl. Enhanced absorption promotes greater generation of photogenerated electron–hole pairs during photocatalysis [22], thereby improving performance. Combined with SEM analysis (Figure 3), EG-BiOCl's microsphere architecture facilitates superior light penetration and multiple reflections [23], further augmenting photocatalytic efficiency.

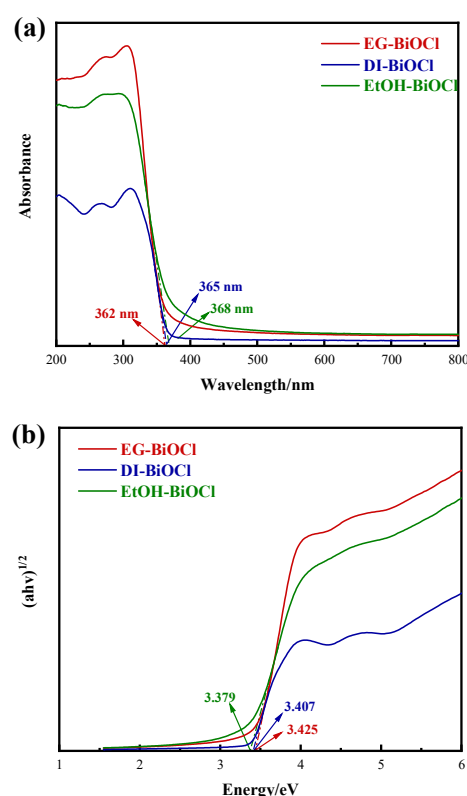


Figure 5. UV-vis DRS diagram (a) and band gap diagram (b) of DI-BiOCl, EtOH-BiOCl, and EG-BiOCl.

3.4. Photoelectrochemical Properties

EIS analyzed charge carrier separation and transfer efficiency in DI-BiOCl, EtOH-BiOCl, and EG-BiOCl. As shown in Figure 6, DI-BiOCl exhibited the largest EIS arc radius, followed by EtOH-BiOCl, with EG-BiOCl showing a marginally smaller radius than EtOH-BiOCl. The arc radii decreased with increasing solvent viscosity. Smaller radii indicate lower

charge transfer resistance and enhanced photocatalytic efficiency. This radius progression (DI > EtOH > EG) aligns with the photocatalytic activity ranking of the samples.

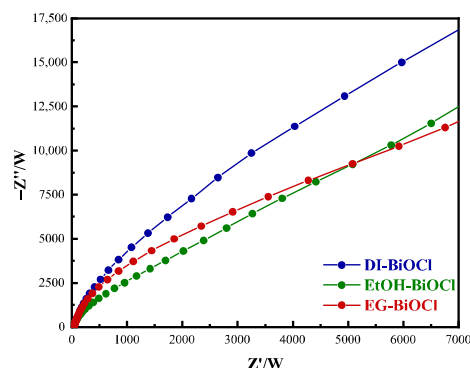


Figure 6. EIS of DI-BiOCl, EtOH-BiOCl, and EG-BiOCl.

3.5. Degradation Performance Evaluation of Photocatalysts

The photocatalytic degradation performance of each sample toward TC-HCl under visible light is shown in Figure 7a. In control experiments, TC-HCl (30 mg/L) remained nearly constant in concentration under both dark and illuminated conditions, confirming its structural stability and resistance to natural photodegradation. Distinct variations emerged upon adding 0.50 g/L of different photocatalysts. After 45 min of dark adsorption and subsequent 60 min visible light irradiation, EG-BiOCl achieved better TC-HCl removal by 76%, attributable to its unique microsphere architecture and greater absorption intensity. In contrast, DI-BiOCl and EtOH-BiOCl exhibited significantly lower removal rates of 18% and 53%, respectively. As shown in Figure 7a, the concentration of TC-HCl remained nearly constant under both dark conditions and visible light irradiation without a catalyst (photolysis), indicating that direct photolysis and self-degradation were negligible.

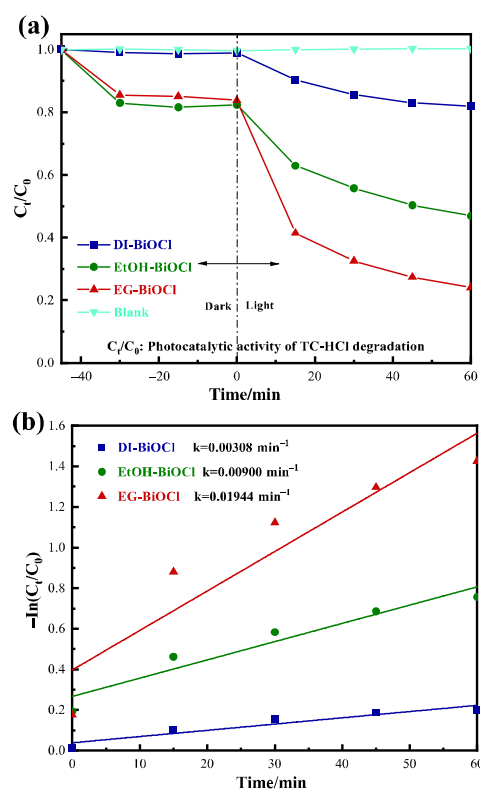


Figure 7. Visible degradation TC-HCl curves of DI-BiOCl, EtOH-BiOCl, and EG-BiOCl (a) and quasi-first-order kinetic fitting (b).

The relationship between $\ln(C_t/C_0)$ and irradiation time (min) was fitted to the pseudo-first-order kinetic model to determine the rate constant k . As shown in Figure 7b, EG-BiOCl exhibited a k value of 0.01944 min^{-1} , which is 6.3-fold and 2.1-fold higher than those of DI-BiOCl (0.00308 min^{-1}) and EtOH-BiOCl (0.00900 min^{-1}), respectively, demonstrating its better photocatalytic activity.

The superior photocatalytic activity of EG-BiOCl can be attributed to the synergistic effects of its unique morphological characteristics and enhanced optoelectronic properties, as revealed by our characterization results. Firstly, the hierarchical microsphere architecture (Figure 3c), self-assembled from numerous thin nanosheets, provides a high specific surface area and abundant active sites for reactant adsorption and surface reactions. Secondly, as confirmed by UV-Vis DRS (Figure 5a), EG-BiOCl exhibited the strongest light absorption intensity among the three samples. Its microsphere structure facilitates superior light harvesting through multiple internal reflections within the 3D structure, thereby promoting the generation of more photogenerated electron-hole pairs. Thirdly, the electrochemical impedance spectroscopy (EIS) results (Figure 6) showed that EG-BiOCl possessed the smallest arc radius, indicating the most efficient separation and transfer of photogenerated charge carriers [24]. This is likely due to the intimate contact between the nanosheets within the microspheres, which shortens the charge diffusion path and reduces recombination losses.

In summary, the significantly enhanced photocatalytic performance of EG-BiOCl is not attributable to a single factor but is a direct consequence of its distinctive microsphere morphology, which collectively enhances light harvesting, provides more active sites, and most importantly, facilitates the highly efficient separation and transfer of photogenerated charges [25]. This multi-parameter enhancement underscores the importance of solvent-mediated morphological control in designing high-performance photocatalysts.

3.6. Analysis of Active Species in Photocatalytic System

To test the photocatalytic activity of the present materials, IPA, SO, and AA were used as scavengers of $\bullet\text{OH}$, h^+ , and $\bullet\text{O}_2^-$ (TC-HCl: 30 mg/L ; photocatalyst: 0.30 g/L), in order to identify the main active species in the photocatalytic system.

As shown in Figure 8, the inhibitory effect of IPA on the photocatalytic degradation of TC-HCl by EG-BiOCl was only 4%, indicating that $\bullet\text{OH}$ was not the main active species in the reaction system. However, the TC-HCl degradation efficiency was significantly reduced from 93% to 66% and 75% in the reaction systems containing AA and SO, respectively. The above results show that $\bullet\text{O}_2^-$ and h^+ were the main active species in the photocatalytic degradation of TC-HCl by EG-BiOCl [26].

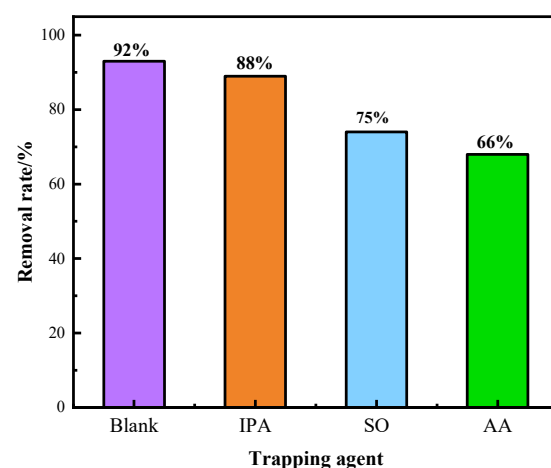


Figure 8. Effect of different scavengers on the photocatalytic activity of EG-BiOCl.

4. Conclusions

This study successfully synthesized DI-BiOCl, EtOH-BiOCl, and EG-BiOCl samples via a one-step solvothermal method. Structural composition and morphological characteristics were analyzed by XRD, FT-IR, XPS, and SEM, and their optoelectronic properties were further characterized using UV-vis DRS and EIS. The photocatalytic performance of DI-BiOCl, ETH-BiOCl, and EG-BiOCl samples prepared with DI, EtOH, and EG as solvents was evaluated by degrading TC-HCl under visible light. TC-HCl is a common antibiotic pollutant in aquatic environments. The main conclusions are as follows:

- (1) Well-crystallized BiOCl materials were prepared, and the influence of different solvents on their photocatalytic performance was investigated. Reaction solvents modulated the microstructure of samples. Compared to DI-BiOCl and EtOH-BiOCl, EG-BiOCl exhibited a unique spherical architecture composed of closely stacked nanosheets with thicknesses below 100 nm. This structural configuration contributes to enhanced photocatalytic activity.
- (2) Solvent selection influenced the light absorption intensity of BiOCl materials but minimally affected their optical response range. DI-BiOCl, ETH-BiOCl, and EG-BiOCl showed similar absorption edges and nearly identical E_g values.
- (3) Following 45 min of dark adsorption and 60 min of visible light irradiation, the EG-BiOCl photocatalyst removed 76% of TC-HCl (30 mg/L). Its rate constant k exceeded those of DI-BiOCl and EtOH-BiOCl by factors of 6.3 and 2.1, respectively.
- (4) Comprehensive characterization confirms that enhanced light absorption intensity and the distinctive spherical architecture synergistically improve photocatalytic performance. These structural advantages confer EG-BiOCl with optimal degradation efficiency.

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Conflicts of Interest: The authors declare no conflicts of interest.

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