

Efficient photoelectrocatalytic degradation of amoxicillin using nano-TiO₂ photoanode thin films:

A comparative study with photocatalytic and electrocatalytic methods

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Abstract

Excessive utilization of antibiotics in human, animal, and aquaculture settings poses a substantial threat to both human health and the environment. Photoelectrochemical processes are increasingly employed due to their ability to mineralize organic compounds and generate oxidizing species, rendering even small water quantities more amenable for utilization. Thus, this study presents the fabrication of an efficient nano-TiO₂ photoanode thin film (PATF) specifically designed for the photoelectrocatalytic (PEC) degradation of amoxicillin (AMX). The TiO₂ PATFs were prepared on fluorine-doped tin oxide (FTO) using an ultrasonic spray pyrolysis process with various titanium isopropoxides acetylacetonate molar ratios (1:1 to 1:10). The PEC oxidation of AMX was investigated using various molar ratios of TiO₂ PATF/FTO by linear sweep voltammetry, and a 1:8 molar ratio of PATF exhibited superior PEC oxidation activity than other TiO₂ PATFs. Subsequently, the PEC degradation efficiency of AMX was compared with that of photocatalytic (PC) and electrocatalytic (EC) methods. The obtained results demonstrated that the PEC procedure effectively eliminated 76.2% of AMX within 120 minutes at 0.8 V, outperforming the removal rates attained by the EC (32.3%) and PC (52.6%). Notably, increasing the voltage to 1.0 V accelerated the PEC degradation of AMX, attaining a removal efficiency of 91.2% within 90 minutes and exceeding 95% within 120 minutes.

Keywords: Nano-TiO₂ thin films; Photoanode; Photoelectrocatalytic oxidation; pharmaceutical pollutant; Degradation

1. Introduction

The abuse of pharmaceuticals has long been associated with the contamination of surface water, thus affecting the purity of water used for drinking, agriculture, and recreation. Antibiotic residues in surface water have significant effects on humans, animals, and plants, contributing to antibiotic resistance and the proliferation of disease-causing microorganisms. Extensive research indicates that approximately 95% of antibiotics are discharged into the environment, heightening concerns regarding the persistence and prevalence of residual antibiotics in aquatic environments with limited biodegradability. Amoxicillin (AMX), the most widely used antibiotic in the world (47% of global antibiotic consumption), is widely used in both human and veterinary medicine, resulting in significant excretion into water bodies. In addition, AMX and its breakdown products have the potential to impair immune systems and alter the intestinal microbiota of humans and animals. In light of the widespread presence of AMX residues in surface water, groundwater, and potable water sources, immediate action is required to eliminate them effectively from aquatic environments. Antibiotic residues in the environment have been mitigated using diverse technologies, including adsorption, filtration, ion exchange, reverse osmosis, biodegradation, and advanced oxidation processes. However, the effectiveness of these strategies varies depending on the particular antibiotic, environmental conditions, and treatment method employed. Due to their recalcitrant nature and complex molecular structure, traditional methods have proven ineffective for removing antibiotic residues from aquatic environments.

Semiconductor-based photocatalysis employing advanced oxidation processes presents a highly effective alternative for the removal of antibiotics. This methodology harnesses primary oxidants and energy sources to generate highly reactive hydroxyl radicals (OH.), which exhibit

remarkable efficiency in degrading antibiotic compounds. To date, several common semiconductors, such as TiO_2 , ZnO , and CdS , have been used to effectively oxidize or degrade AMX. TiO_2 has been extensively utilized in the photocatalytic removal of various pollutants, including antibiotics, due to its low cost, greater electron conductivity, superior stability, and non-toxicity. Furthermore, TiO_2 has a high reaction rate and can operate at wide range of pHs and irradiation wavelengths, making it a suitable candidate for photocatalytic oxidation and degradation of antibiotics. Unfortunately, the high level of recombination between the photo-generated electrons and holes TiO_2 limits its performance. To solve this problem, a combination of photochemical and electrochemical processes can slow or stop the rapid recombination of the electron/hole pairs formed during the process. In addition, the photoelectrochemical (PEC) system can allow for efficient charge separation, thereby generating free radicals that can degrade the target pollutants. Recent studies have demonstrated that TiO_2 semiconductor-based photoanodes are effective in photoelectrochemically degrading a variety of organic compounds, including pharmaceuticals. This enhanced performance is attributable to the higher optical absorption of TiO_2 semiconductor thin films, which results in excellent visible light absorption. Additionally, the stability of the TiO_2 semiconductor-based photoanode is considerably greater than that of other photoanode materials, making them more suitable for long-term applications.

In the present work, we fabricated TiO_2 thin-films on fluorine-doped tin oxide glass using ultrasonic spray pyrolysis with different molar ratios of titanium isopropoxides and acetylacetonone precursors. The fabricated TiO_2 photoanodes were characterized by various physicochemical techniques and utilized for PEC degradation of AMX for the first time. The fabricated photoanode film is a more suitable for the PEC degradation of AMX (1.0 V vs. SCE) than photocatalytic and

electrocatalytic methods. Other essential parameters such as effect of applied potential strategy for removing persistent organic pollutants from contaminated water are elucidated.

2. Experimental

2.1. Fabrication of TiO₂ photoanode films on FTO

TiO₂ thin films were deposited onto FTO glass substrates via ultrasonic spray pyrolysis with minor modifications to a previously reported procedure. In summary, a mixture of 0.2 M titanium (IV) isopropoxide (97.0%) and variable molar ratios of acetylacetone (1:1 to 1:10) was prepared. The volume of the solutions was then adjusted to 60 mL by adding ethanol, and they were agitated at room temperature for one hour. At a flow rate of 5 L/min, compressed air was utilized to convey the ultrasonic generator's aerosol. TiO₂ was deposited onto the FTO glass substrate at 350°C, followed by an hour of annealing at 500°C in an air atmosphere. Our earlier studies provide additional information regarding the investigation of TiO₂ thin films with different molar ratios of titanium (IV) isopropoxide:acetylacetone. Based on our photoelectrocatalytic (PEC) experimental results, the TiO₂ thin film fabricated using a titanium (IV) isopropoxide:acetylacetone precursor with a molar ratio of 1:8 was found to have the highest photodegradation performance and thus it was chosen for further surface characterizations.

2.2. Characterization

The surface morphology and cross-sectional images of the samples were obtained by scanning electron microscope (SEM); Quanta 250 ESEM. Elemental analysis (EDX) was also performed in a focused ion beam-equipped SEM (Quanta 3D FIB). Films thickness and structure nature are estimated by transmission electron microscopy (TEM) and high-resolution transmission electron

microscopy (HRTEM), performed in a Tecnai system and Titan system at 200 kV and 300 kV, respectively. X-ray diffraction characterizations for determining structural properties were investigated via Bruker D2 Phaser XRD for radiation of, 30 kV, at 10 mA. The XRD diffractogram of each sample was measured in 2 theta configurations between 10 and 80, with 0.08 step angle and 0.5 s step time for a total of 1000 steps. The structure of the films was also characterized by Raman spectroscopy (Witec Alpha 300 RAS) at a wavelength of 532 nm using x 50 L objective lens.

2.3. Photoelectrochemical experiments

The PEC measurements including LSV were performed using a VMP-300 (BioLogic Instruments, US) electrochemical workstation with three electrode configuration set-ups. The 4 cm × 7.5 cm TiO₂/FTO was used as the working electrode, while the Pt sheet and the saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. For the PC and PEC measurements, the Xenon Lamp (AM 1.5, 350 W Xe, = 250–1100 nm, 100 mW cm²) was used as the light source. LSV for the PEC oxidation of AMX at various TiO₂/FTO electrodes was performed by scanning the potential from 0 to 1.5 V at a scan rate of 10 mV/s. Under illumination, a PEC oxidation of TiO₂ thin films was analyzed in a 100 mL electrochemical cell containing 20 mg/L of AMX and citric acid. Every 10 minutes, a sample was collected and analyzed using UV-VIS spectroscopy. The effect of varying cell potential (0 to 1.2 V) on the PEC of AMX with TiO₂/FTO films was investigated. In addition, five consecutive recycle PEC measurements were performed at 1.0 V in 1 M Na₂SO₄ electrolyte solution over the fabricated electrode.

3. Characterization

3.1. Surface characterization of fabricated TiO₂ thin-films

The surface morphology of the TiO₂ thin film was analyzed using TEM and SEM, and the representative images are displayed in Fig. 1. The SEM image of the TiO₂ thin film reveals more smoother, uniform and crack-free surface of well-interconnected nano-particles (Fig. 1A). TEM analysis (Fig. 1B) revealed that the manufactured TiO₂ thin film has a thickness of approximately 370 nm and an average diameter of approximately 14 nm. Also, the fringes associated with the {101} facet for anatase form of TiO₂ are clearly visible from the TEM in Fig. 1C. The SAED pattern corresponding to the (101) plane of the anatase crystal structure is depicted in Figure 1D as a dazzling diffraction ring from the interior of the crystal structure.

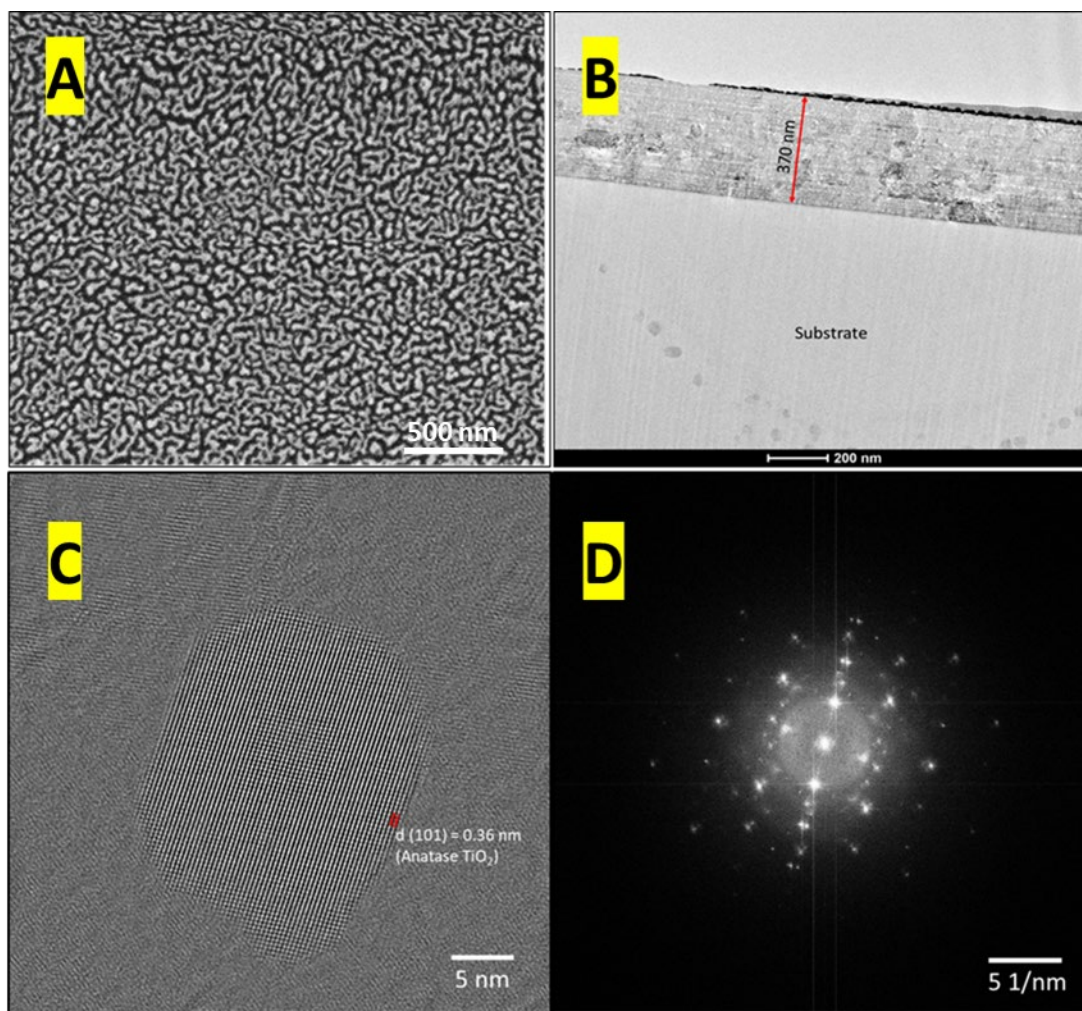


Fig. 1. A) SEM, TEM (B) and HRTEM (C) images and SAED pattern of as-fabricated TiO₂ thin film.

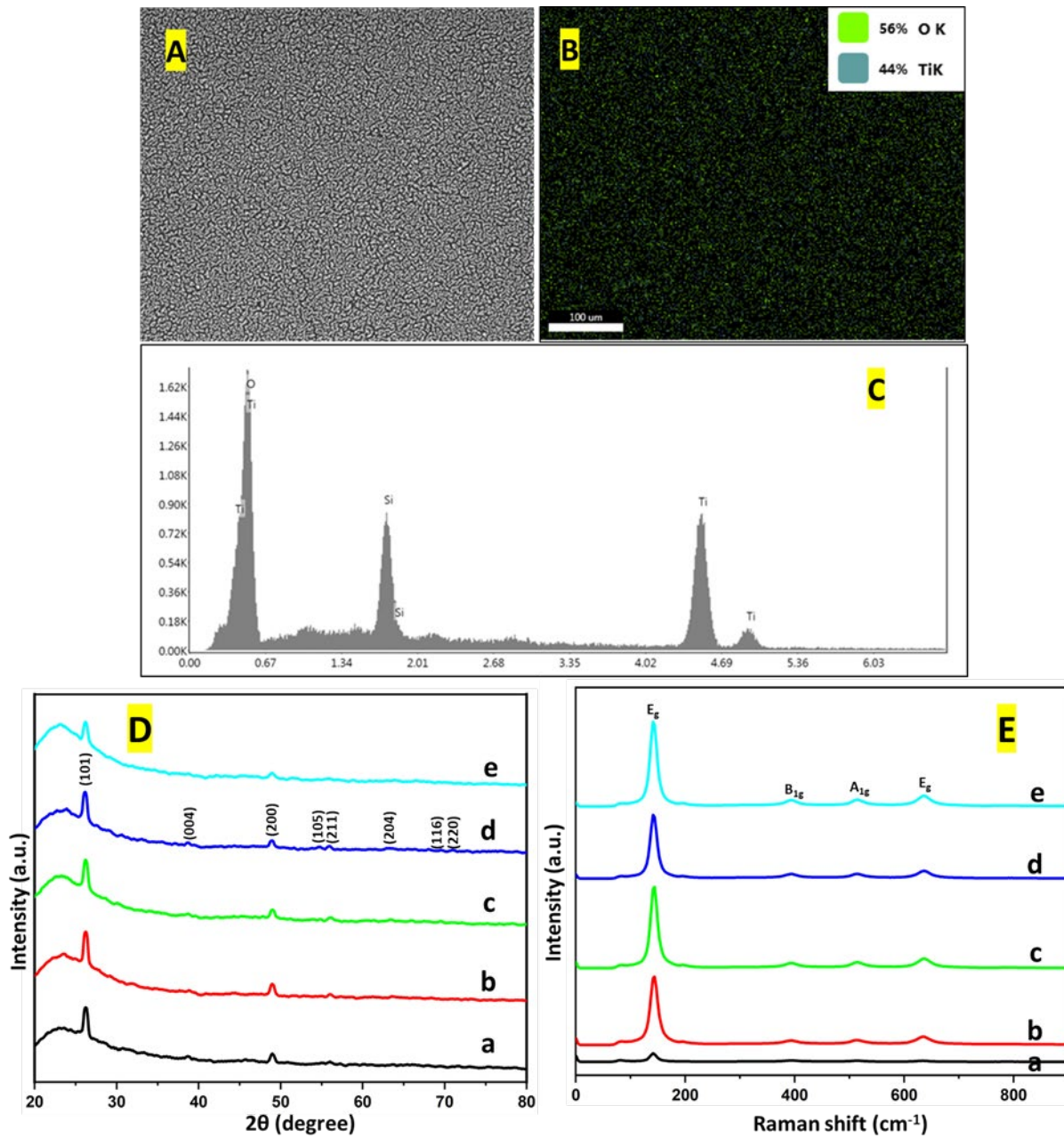


Fig. 2. A) SEM, elemental mapping (B) and EDX spectrum (C) of TiO₂ thin film. D) XRD and Raman spectrum of different molar ratio of titanium (IV) isopropoxide:acetylacetonate precursor (a=1:1, b=1:3, c=1:5, d=1:8, e=1:10) prepared TiO₂ thin films.

Figures 2B and C depict the elemental mapping and EDX spectrum for the TiO₂ thin film (Figure 2A) that was manufactured. In both the elemental mapping and EDX spectrum, only the signals of metallic Ti and O were detected, confirming the purity of the TiO₂ thin film. Analysis of the modified TiO₂ films crystallinity and phase composition was conducted by XRD, where the diffractogram for samples from 1:3 to 1:20 (a-e) is illustrated in Figure 2D. The diffraction peaks at 2 theta of 25.3° and 48.1°, which correspond to the reflection planes of (101) and (200), reveal the anatase TiO₂ structure. The unit cell lattice constants of the films are reported in Table 1, which reveals that anatase is the dominant phase. Overall, all the produced films were annealed at the same temperature, and an increase in the amount of unchelated acetylacetonone in the precursor solution has no direct impact on the structural characteristics of TiO₂ thin films. Figure 2E depicts the Raman spectrum of all prepared films (1:1 to 1:20, a-e). The exhibited Raman modes are typical of the D_{2d} point group and can be attributed to the Raman spectra of TiO₂ anatase structure: 148 cm⁻¹ = E_g, 198 cm⁻¹ = E_g, 398 cm⁻¹ = B_{1g}, 523 cm⁻¹ = A_{1g}, 524 cm⁻¹ = B_{1g}, and 642 cm⁻¹ = E_g [35]. Clearly the complex forms at a molar ratio of 1:2, and beginning at a ratio of 1:3, an excess of acetylacetonone may be observed in the solution, indicating that the molar ratio of 1:1 is insufficient for complete complex formation [25]. Thus, mixing acetylacetonone with TiO₂ increased the Raman intensity of the films and altered the surface. As mentioned above, the fabricating rate of 1:10 titanium (IV) isopropoxide:acetylacetonone ratio was slower compared to the remaining prepared films, thereby the vibrational bands of this sample showed lower intensities. Thus, all findings indicates that the 1:8 molar ratio of titanium (IV) isopropoxide:acetylacetonone precursor prepared TiO₂ thin film has more uniform and superior characteristics than others films, and hence it is used for the further PEC studies.

3.2. Photoelectrochemical degradation of AMX using TiO₂ thin film

The PEC oxidation of AMX was studied using LSV in order to evaluate the photoelectrocatalytic activity of the as-prepared TiO₂/FTO photoanodes. The LSV studies of the different molar ratio of titanium (IV) isopropoxide:acetylacetonone precursor prepared TiO₂/FTO were examined in potential scanning from 0 to 1.5 V at 10 mV/s scan rate in 0.1 M NaSO₄ electrolyte solution containing 20 mg/L of AMX in the absence of light irradiation. As shown in **Fig. 3A**, a well-defined oxidation peak was observed at 0.46 V using investigated TiO₂ thin films, and is due to the oxidation of AMX on the TiO₂ photoanodes. In addition, the film consisting of 1:8 (TTIP:Acac) molar ratio had the most photocurrent response than other investigated TiO₂ thin films. Hence, sample 1:8 has the highest PEC oxidation activity and optimal photocatalytic performance amongst other molar ratios. We have also performed LSV of the thin film electrode in 0.1 M NaSO₄ electrolyte with 20 mg/L of AMX under illuminated and dark conditions. As shown in **Fig. 3B**, the modified thin-film electrode exhibits a greater photocurrent response under illuminated conditions than dark conditions. This indicates that the TiO₂ photoanode electrode produced a greater number of OH radicals under illuminated conditions by separating more charge carriers. Thus, photoanode material as-prepared is more suitable for PEC degradation of AMX. In order to confirm the PEC degradation performance, the dark adsorption, photocatalysis (PC) and electrocatalysis (EC) of AMX were conducted and the obtained results are displayed in **Fig. 3C**. Typically, scavengers are added to remove or de-active unwanted reaction products, here we utilized 0.1 M citric acid to reduce agglomeration and improve the suspension's stability. In the absence of light, the photoanode's degradation efficiency towards AMX was negligible. The degradation efficiency was improved to 32.3% in 120 min (applied potential of 0.8 V) under EC

using TiO₂ photoanode. while under PC condition, the degradation efficiency of CS was greatly improved 52.6% in 180 min under PC to, indicating that the fabricated electrode has excellent catalytic activity towards AMX in both EC and PC conditions. However, the highest catalytic activity of photoanode towards AMX was found in PEC process, where 76.2% of AMX was degraded under PEC for 120 min. The above results confirmed that the fabricated TiO₂ photoanode has highest catalytic activity against AMX under PEC conditions than others.

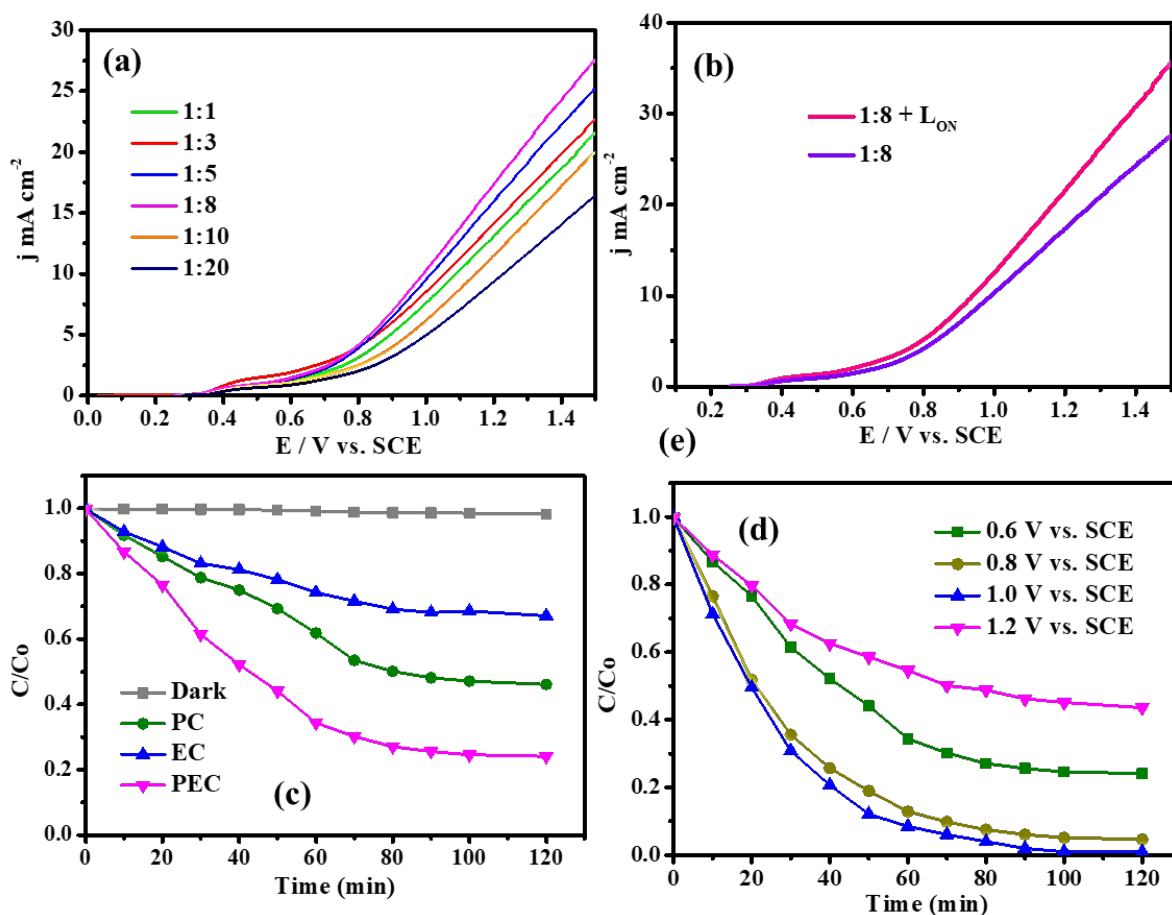


Fig. 3. (a) LSV of different molar ratio of titanium (IV) isopropoxide:acetylacetonate precursor prepared TiO₂ photoanode in 0.1 M NaSO₄ electrolyte solution containing 20 mg/L of AMX at the scan rate of 10 mV/s. b) At similar conditions, LSV of response of TiO₂ photoanode in the absence and presence light illumination. C) Degradation of AMX (20 mg/L) using TiO₂ photoanode under

dark, photochemical, electrochemical, and PEC conditions (vs. 0.8 V applied potential) for 0–120 min. d) PEC degradation of AMX using TiO₂ photoanode at various applied potentials from 0.6 to 1.2 V for 120 mins.

To determine the optimal potential for the PEC, identical PEC conditions were conducted for 120 min at various applied potentials spanning from 0.6 to 1.2 V for degradation of AMX. The fabricated photoanode exhibits remarkable photodegradation efficiency (91.2% in 90 min and 95.6% in 120 min) for AMX at 1.0 V versus RHE. In addition, when the applied potential was less than 1 V, the photodegradation efficiency decreased dramatically. Notably, when the applied potential was 1.2 V, the efficacy of the fabricated photoanode electrode degraded by 100 percent. Nevertheless, we have chosen 1.0 V as the optimal potential for PEC investigations, as HER evaluations are performed at potentials greater than 1.0 V. Fig. 4 depicts the detailed mechanism for the photodegradation of AMX by TiO₂ photoanode. TiO₂ anatase has a band gap of 3.2 eV and is activated by ultraviolet light ($\lambda = 387$ nm). By radiating light with the corresponding wavelength, electrons are transmitted from the valence band to the conduction band. When electrons absorb light energy and migrate into the conduction band, electron-hole pairs form. Excited electrons can undergo single electron reduction into the superoxide radical anion, O₂^{•-}, in the presence of oxygen. These electron vacancies (h⁺) are then able to react with H₂O to generate hydroxyl radicals (OH[•]). These radicals are extremely reactive and mineralize AMX to form intermediates. The formed intermediates are then further oxidized to produce CO₂ and H₂O, which are released into the atmosphere.

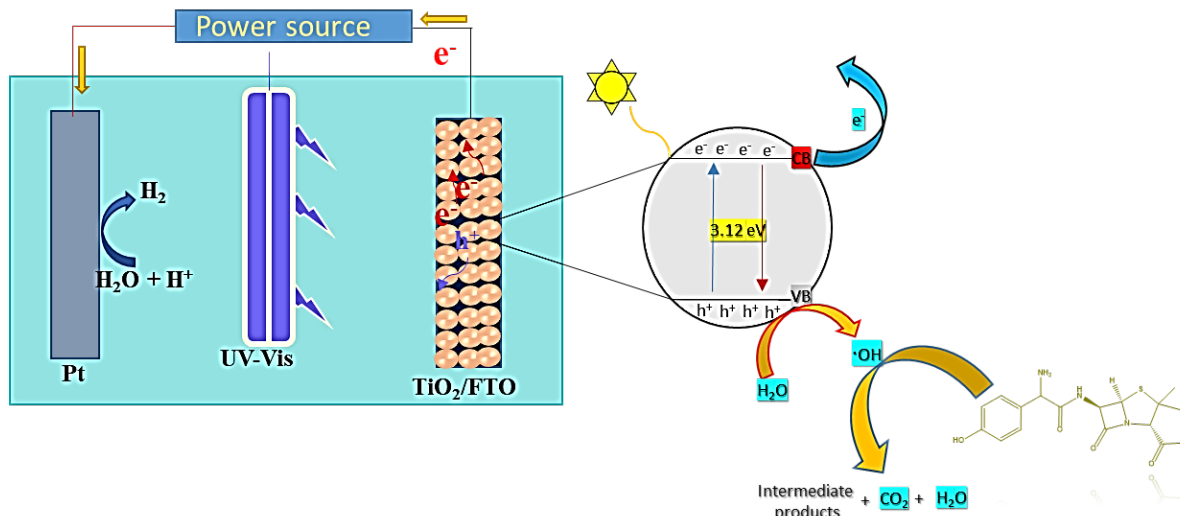


Fig. 4. The plausible PEC mechanism for the degradation of AMX by TiO₂ photoanode.

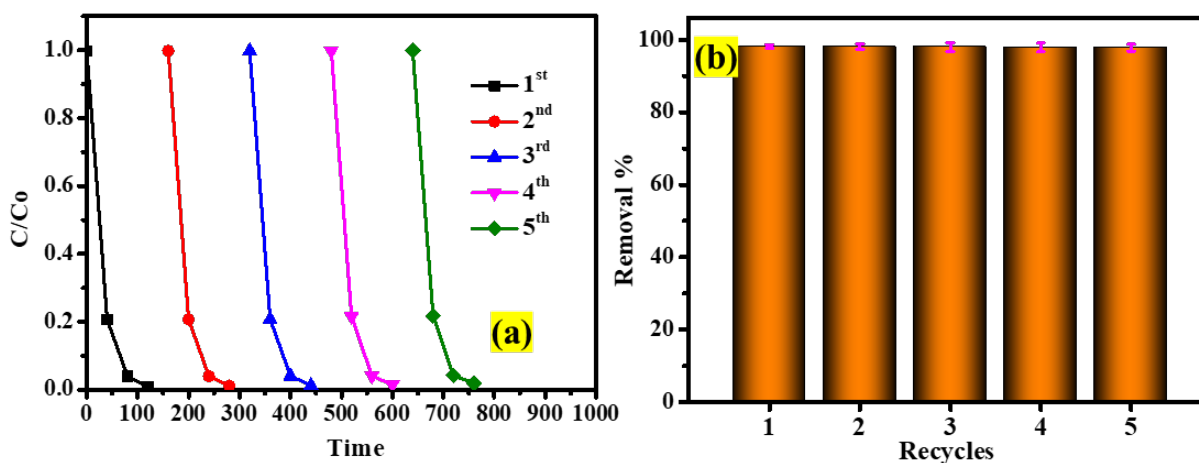


Fig. 4. a) The PEC recycle experiments and b) corresponding removal efficiency of AMX by TiO₂ photoanode.

A PEC experiment was conducted to test TiO₂ reusability for AMX degradation. The results of five consecutive reaction cycles are shown in **Fig. 5A**. It is apparent that the AMX removal rates remained relatively high after five cycles of the fabricated TiO₂ photoanode. The results demonstrated that synthesized TiO₂ has significant reusability for AMX degradation in the PEC process. As shown in **Fig. 5B**, the fabricated photocathode retained 98.2% of AMX removal after

five cycles, indicating that TiO_2 is well suited to prolonged AMX degradation with high efficiency. In addition, these results suggest that TiO_2 is an appropriate material for this purpose, as it can provide efficient and long-term water purification.

5. Conclusion

In conclusion, the PEC oxidation of amoxicillin (AMX) was studied using different molar ratios of titanium isopropoxides and acetylacetonate precursor-prepared TiO_2 thin films. The TiO_2 photoanode thin films were prepared through ultrasonic spray pyrolysis. The surface and spectroscopic characterization of the fabricated 1:8 TiO_2 thin films revealed the presence of the anatase phase and the uniform deposition of the thin film on the FTO. Moreover, the results revealed that the 1:8 molar ratio TiO_2 thin film exhibited significantly higher photocurrent density and AMX degradation rates than other molar ratios. This demonstrated that the 1:8 molar ratio thin film is a suitable photoanode for the PEC degradation (at 1.0 V vs. SCE) of AMX. The PEC conditions showed enhanced degradation efficiency of AMX using TiO_2 thin film compared to photocatalytic and electrocatalytic conditions. Also, the fabricated photoanode has excellent degradation ability (>91% in 90 min) towards AMX with appropriate reusability. These photocatalysts would effectively degrade AMX and provide a novel strategy for removing persistent organic pollutants from contaminated water.