1 **ZnO/TiO₂/Ag₂Se nanostructures as photoelectrocatalysts**
2 **for the degradation of oxytetracycline in water**

3 Katherina Changanauquí ^{a,b}, Enric Brillas ^{a,1}, Hugo Alarcón ^b, Ignasi Sirés ^{a,*,1}

4 ^a *Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química*
5 *Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028*
6 *Barcelona, Spain*

7 ^b *Centro de Desarrollo de Materiales Avanzados y Nanotecnología, Universidad Nacional de*
8 *Ingeniería, Av. Túpac Amaru 210, Rímac, Lima, Peru*

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10 * Corresponding author: E-mail address: i.sires@ub.edu (I. Sirés)

11 ¹ Active ISE member

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Abstract

Optimized thin films composed of ZnO nanorods, grown after preliminary electrodeposition and successively coated with 3 layers of TiO₂ and decorated with Ag₂Se nanoparticles, were prepared onto glass FTO wafers to treat oxytetracycline solutions by photoelectrocatalysis (PEC). The coatings were thoroughly characterized by XRD, Raman and UV/Vis diffuse reflectance spectroscopy, confocal microscopy, FE-SEM, HRTEM, EDX and XPS. The synthesized films had a mean thickness of 1.19 μm , length > 500 nm and a bandgap of 1.85 eV, being visible-light photoactive. Good stability and reproducibility was obtained when treating 5 mg dm⁻³ oxytetracycline solutions in 0.050 M Na₂SO₄ at pH 5.8, attaining 96.5% antibiotic decay after 360 min at an anodic potential of +1.0 V vs Ag|AgCl under irradiation with a 36-W blue LED lamp. Comparative photocatalysis and electrochemical oxidation treatments revealed an interference between the active sites where the oxidant species were generated, causing an efficiency loss in PEC. The antibiotic was also removed from urban wastewater, thanks to the additional attack of electrogenerated active chlorine, although at a slower rate due to parallel oxidation of the natural organic matter. A degradation route for oxytetracycline is proposed based on the five primary products detected by LC-QToF-MS.

Keywords: Antibiotic; LED lamp; Nanocomposites; Photoanode; Photoelectrocatalysis; Visible light

1. Introduction

Oxytetracycline (OTC, $C_{22}H_{24}N_2O_9$) is a broad-spectrum antibiotic commercially available since 1950. It belongs to the family of tetracyclines, which is effective against a wide range of microorganisms including Gram-positive and Gram-negative bacteria, rickettsiae and protozoan parasites, among others, as a result of protein synthesis inhibition and hence, growth prevention. OTC serves as a cure to many infections in humans and animals, such as pneumonia, chronic bronchitis or urethritis, as well as to promote the growth in livestock [1]. Owing to its worldwide use, OTC has been detected within the $\mu\text{g L}^{-1}$ range in soil [2,3], surface water [4-8] and wastewater treatments plants [9]. Its presence in the aquatic environment can be dangerous due to its potential toxicity, alongside carcinogenicity, mutagenicity and endocrine disruption. Furthermore, it is related to the promotion of antibiotic-resistant bacteria (ARBs) [10,11]. Aiming at its destruction from aqueous solutions, several authors have evaluated the performance of photolytic action of gamma [12] and UVC [13,14] radiation, as well as the additional oxidation with the strong oxidant hydroxyl radical ($\cdot\text{OH}$) originated via an advanced oxidation process (AOP) like UV/ H_2O_2 [1,13-15]. Greater effectiveness has been shown by other AOPs such as photo-Fenton [16], heterogeneous Fenton-like [17-19], and photocatalysis (PC) under UV, visible or solar irradiation with $\text{ZnO/CdS/Graphene oxide}$ [20], ZnO/ZnWO_4 [21], carbon nanotubse/ BiVO_4 [22] and $\text{TiO}_2/\text{Graphene oxide}$ [23] composites as photoanodes. In contrast, research about electrochemical AOPs (EAOPs) is much more scarce. OTC solutions have been treated by electrochemical oxidation (EO) with IrO_2 [24], boron-doped diamond (BDD) [25] and $\text{Ti-Sn-Sb}/\gamma\text{-Al}_2\text{O}_3$ [26] anodes, and by photoelectrocatalysis (PEC) using $\text{Cu}_2\text{O}/\alpha\text{-Fe}_2\text{O}_3$ [27] and $\text{Ag}_3\text{PO}_4/\text{BiVO}_4$ [28] photoanodes.

PEC is a hybrid method that combines the simultaneous action of PC and EO to remove small contents of organic pollutants from water [29,30]. In this EAOP, a thin-film

semiconductor photoanode placed in an electrolytic cell is irradiated with photons with greater energy than the bandgap (E_{gap}). As a result, electrons can jump out from the valence band of the semiconductor to its conduction band (e^-_{CB}), yielding a hole in the former (h^+_{VB}) according to reaction (1). The generated h^+_{VB} can then oxidize water at the photoanode surface (P) to form adsorbed $\bullet\text{OH}$ from reaction (2). However, in the absence of applied current (i.e., PC conditions), the $e^-_{\text{CB}}/h^+_{\text{VB}}$ pair quickly disappears upon recombination reaction (3), causing a significant decrease of the oxidation ability [31-33]. This drawback is overcome in PEC by applying a small anodic potential (E_{bias} or E_{an}) to the photoanode, which favors the spatial separation of both charge carriers because of the transport of e^-_{CB} to the cathode of the cell, ending in a higher $\text{P}(\bullet\text{OH})$ production. This oxidant can be additionally generated upon direct water oxidation at the photoanode surface via reaction (4) (i.e., EO conditions) [34].

Anatase TiO_2 is the most widely used photocatalyst in PC and PEC due to its large photoactivity and photostability, but since its bandgap is relatively large ($E_{\text{gap}} = 3.2 \text{ eV}$, $\lambda = 387.5 \text{ nm}$) it requires UV light to be photoexcited, which is a drawback because the UV range only represents about 3-5% of the solar spectrum [29,30]. Two main strategies have been recently followed to improve the effectiveness of this non-toxic and cheap material: (i) the fabrication of TiO_2 -based nanostructures with large surface area that provide more active sites for $e^-_{\text{CB}}/h^+_{\text{VB}}$ generation via reaction (1) [35,36], and (ii) the modification of TiO_2 with

transition metals or the preparation of heterostructures by decoration with noble metals such as Ag [37] and Au [38,39], which extend the photon absorption to the visible light range.

Many semiconductors have been used as photoanodes. This is the case of ZnO, which is a cheap and environmentally friendly material whose $E_{\text{gap}} = 3.4$ eV also allows photoexcitation in the near-UV spectral region. It can be prepared as a transparent thin film that enhances the photoexcitation efficiency, and in the form of ZnO nanorods (NRs) it provides a large surface area [29,40-41]. Several authors have reported that the PEC treatment of organics can be even more effective using ZnO instead of TiO₂ [42]. The main drawback of ZnO as photoanode is its higher tendency to photocorrosion, which can be limited by using composites with semiconductors like TiO₂ and other metal oxides that yield a stable heterojunction, eventually favoring the separation of photogenerated $e^-_{\text{CB}}/h^+_{\text{VB}}$ pairs [43,44]. The ZnO/TiO₂ heterostructure cannot absorb visible light either, owing to the high E_{gap} of both components and hence, another heterojunction with a semiconductor with lower E_{gap} is required. Ag₂Se seems a suitable material for this, since it has a low $E_{\text{gap}} = 1.8$ V [45,46]. It behaves as a super ionic conductor at high temperature and it is used in magnetic field sensing devices, but it has never been applied to water contaminated by PEC.

This work reports the synthesis and thorough characterization of thin-film nanocomposites on fluoride-doped tin oxide (FTO). ZnO NRs were first grown, followed by coating with several TiO₂ layers to form a heterojunction giving more stability to ZnO against photocorrosion. The film was finally decorated with Ag₂Se nanoparticles by electrodeposition. The oxidation ability of ZnO/TiO₂/Ag₂Se thin-film photoanodes prepared under different conditions has been tested from PEC treatments of 5 mg L⁻¹ OTC solutions in sulfate medium at natural pH, with illumination provided by a blue LED lamp. Comparative assays by PC and EO were performed, and the effect of E_{an} , irradiation source and water matrix on pharmaceutical decay was analyzed. The primary products accumulated during the

PEC treatments were identified by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF-MS), allowing the proposal of a degradation route for OTC.

2. Experimental

2.1. Chemicals

OTC hydrochloride (> 95% purity) was purchased from Sigma-Aldrich. FTO glass TEC7 wafers (2.2 mm thick, $7 \Omega \text{ sq}^{-1}$ resistance) were purchased from Dyesol Australia. Na_2SO_4 used as supporting electrolyte was of analytical grade purchased from Fluka. High-purity water (Millipore Milli-Q, resistivity > $18.2 \text{ M}\Omega \text{ cm}$) was employed to prepare most of the solutions, although some degradation trials were carried out employing the secondary effluent of a municipal wastewater treatment plant. The rest of chemicals of HPLC or analytical grade were purchased from Merck, Sigma-Aldrich, Panreac and Alfa Aesar.

2.2. Synthesis of thin-film photoanodes

Before coating, the FTO conductive substrates ($2.5 \text{ cm} \times 2.0 \text{ cm}$) were ultrasonically cleaned in 0.10 M NaOH, ultrapure water and acetone, being further rinsed with water. The preparation of ZnO NRs thin films onto the conductive side of FTO was made by modifying a previous procedure [47-49]. The nucleation of $\text{Zn}(\text{OH})_2$ seeds was first studied by chronoamperometry in an electrolytic cell equipped with the FTO as the cathode, a Pt wire as the anode and Ag|AgCl (3 M KCl) as the reference electrode. The cell contained 50 cm^3 of a solution composed of 0.10 mM $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.10 M NaNO_3 and 4 g dm^{-3} poly(vinylpyrrolidone) (PVP) at 70°C . Under these conditions, the cyclic voltammogram of Fig. 1a shows an irreversible reduction peak R_1 at a cathodic peak potential (E_p^c) of -1.1 V vs Ag|AgCl, which can be ascribed to the reduction of NO_3^- to NO_2^- ion with formation of OH^- ion. This caused the precipitation of $\text{Zn}(\text{OH})_2$ at the cathode, which could be subsequently dehydrated to ZnO at 70°C [47,50,51]. Based on this finding, the chronoamperometric

deposition of Zn(OH)₂ seeds was performed at a constant cathodic potential (E_{cath}) of -1.1 V vs Ag|AgCl for 180 s. The resulting hydroxide was then calcined at 400 °C for 2 h, and the ZnO NRs were obtained by hydrothermal treatment at 90 °C for 75 min upon immersion in the supernatant solution resulting from a 0.15 mM Zn(NO₃)₂•4H₂O solution in 0.80 M NaOH [49].

The TiO₂ coating over the above FTO/ZnO NRs thin film was prepared by modifying a previous procedure [52]. An alkaline colloidal TiO₂ suspension was prepared with 3.3 mM Ti(IV) isopropoxide, 0.013 mM 2-propanol and 0.010 mM diethanolamine at pH 11 and ambient temperature. The FTO/ZnO film was immersed in 50 cm³ of this suspension at a rate of 5 cm min⁻¹, coated for 10 min and retrieved again at 5 cm min⁻¹. This sequence was repeated one or two times to obtain 2 or 3 coatings, and the photoanodes obtained were so-called ZnO/TiO₂(2) and ZnO/TiO₂(3), respectively. After each cycle, the sample was dried at 100 °C for 10 min, followed by calcination at 550 °C for 1 h.

The decoration of the FTO/ZnO/TiO₂ composites with Ag₂Se nanoparticles was made through a procedure modified from Chen et al. [53]. A preliminary electrochemical study was made by chronoamperometry using the same three-electrode cell with 100 cm³ of a solution containing 0.50 M KSCN, 5.0 mM AgNO₃, 2.5 mM H₂SeO₃ and 0.05 M KNO₃ at pH 3.0 and 25 °C. Fig. 1b depicts two consecutive cyclic voltammograms recorded for this system with a ZnO/TiO₂(3) working electrode, at 50 mV s⁻¹. The cathodic scan of the first cycle shows three consecutive irreversible reduction peaks, R₁, R₂ and R₃, with E_p^c values of -0.36, -0.44 and -0.60 V vs Ag|AgCl, respectively. The R₁ peak corresponds to the monoelectronic reduction of the Ag(SCN)_n¹⁻ⁿ complexes to Ag from reaction (5); the R₂ peak, to the reduction of HSeO₃⁻ to Se via reaction (6); and the R₃ peak, to the Ag₂Se formation from reaction (7) [53]. The overall reduction process is given by reaction (8). The R₂ peak was slightly shifted to more negative potentials in the second cycle, which can be related to the Ag₂Se direct formation

from Ag oxidation and HSeO_3^- reduction by reaction (9). In the anodic scan, two consecutive irreversible oxidation peaks, O_1 and O_2 , with anodic peak potentials (E_p^a) of -0.01 and +0.19 V vs Ag|AgCl, were found. They can be associated with the oxidation of Ag and of the Se-Se bond in Ag_2Se , respectively [50].

Once the electrodeposition conditions were clarified, the FTO/ZnO/TiO₂ composites were coated with Ag₂Se nanoparticles by applying an $E_{\text{cath}} = -0.65$ V vs Ag|AgCl for 600 or 900 s. The resulting electrodes were rinsed with Milli-Q water and dried at room temperature. Hereby, the photoanodes are distinguished by indicating the deposition time. For example, ZnO/TiO₂(3)/Ag₂Se(600) accounts for the deposition of 3 layers of TiO₂ followed by Ag₂Se deposition for 600 s. An analogous procedure was used to prepare ZnO/Ag₂Se electrodes. The synthesis procedure for each working electrode is collected in Table S1.

2.3. Degradation of oxytetracycline in aqueous matrices

EO and PEC trials were carried out in a jacketed, undivided three-electrode glass cell containing a synthesized thin film as the anode or photoanode, a Pt wire as the cathode and Ag|AgCl (3 M KCl) as the reference electrode. All the potentials given in this work are referred to this electrode. Solutions of 100 cm³ of 5 mg dm⁻³ OTC with 0.050 M Na₂SO₄ at natural pH 5.8 were potentiostatically electrolyzed at $E_{\text{an}} = +1.0$ V vs Ag|AgCl at 25 °C under magnetic stirring. PEC tests were made by illuminating the catalyst surface with a Higrrow 36-W blue LED lamp (18 × 2 W), placed at about 7 cm from the catalyst and whose irradiance

was 173 W m^{-2} as determined by actinometry at $\lambda_{\text{max}} = 450\text{-}460 \text{ nm}$. Different photoanodes were utilized, which were cleaned with Milli-Q water after use. Some PEC assays were performed with 5 mg dm^{-3} OTC spiked into urban wastewater. For comparison, some PEC experiments were made wither at $E_{\text{an}} = +1.2 \text{ V}$ vs Ag|AgCl or under irradiation with a Sun9x Plus 36-W semicircular UVA lamp ($18 \times 2 \text{ W}$, $\lambda_{\text{max}} = 360 \text{ nm}$) with similar irradiance surrounding the cell and illuminating the catalyst surface. PC assays were carried out in sulfate medium with the blue LED lamp, without current supply. In all photoassisted processes, the entire setup was placed inside a mirror box to enhance the photon collection.

2.4. Procedures and characterization techniques

The synthesized thin films were characterized by several physicochemical techniques. Their crystalline structure was elucidated by X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer, with Cu K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$) and a 2θ scan from 20° to 70° (at $1^{\circ} \text{ min}^{-1}$). Raman spectra used to determine the vibrational modes were obtained with an XploRA PLUS microscope from HORIBA Scientific operating with a laser at 785 nm . Confocal microscopy, used to determine the film thickness, was carried out with a Leica DCM 3D microscope with magnification of $50\times$, field of vision of $254.64 \mu\text{m} \times 190.90 \mu\text{m}$, optical resolution of 0.16 nm and vertical resolution $< 3 \text{ nm}$. UV/Vis diffuse reflectance spectroscopy (DRS), used to determine the E_{gap} , was carried out with a SPECORD 205 UV/Vis spectrophotometer with integrated sphere from Analytik Jena AG within the wavelength range of $300\text{-}800 \text{ nm}$ and the data were processed with WinASPECT 2.0 software. The surface morphology was analyzed by field emission scanning electron microscopy (FE-SEM) using a Carl Zeiss AG Supra 40 microscope. The atomic structure of the samples was studied by high-resolution transmission electron microscopy (HRTEM) using a JEOL JEM-2100 LaB6 microscope with energy-dispersive X-ray spectroscopy (EDX), operating at 200 kV in STEM mode with a dark field detector and a beam size of around 15

nm. The spectrometer was an Oxford Instruments INCA x-sight detector and the data were analyzed with Digital Micrograph software. The elemental mapping was obtained by EDX using INCA Microanalysis Suite version 4.09 software. For these assays, films were scratched out from the FTO substrate. The chemical states of the elements in the film surface were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI 5500 Multitechnique System from Physical Electronics.

The pH of all solutions was measured with a Crison GLP 22 pH-meter. A Metrohm Autolab M204 potentiostat-galvanostat was utilized for chronoamperometric depositions and potentiostatic electrolyses. Prior to analysis, samples were filtered with 0.45 μm PTFE filters from Whatman. The OTC concentration abatement was monitored by reversed-phase high-performance liquid chromatography (HPLC) using a Waters system. It was composed of a 600 LC fitted with a BDS Hypersil C18 5 μm (250 mm $\times$ 4.6 mm) column at 35 $^{\circ}\text{C}$, and coupled to a 996 PAD set at $\lambda = 357.8$ nm. The mobile phase was a 40:60 (v/v) $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (0.010 M KH_2PO_4) mixture at pH 3.0 eluted at 0.6 $\text{cm}^3 \text{min}^{-1}$. OTC was detected at a retention time (t_r) of 6.3 min with a limit of quantification of 0.1 mg dm^{-3} . The data were analysed with Empower Pro software, and average values are plotted in figures.

The primary aromatic products formed during the PEC treatments of OTC were identified by LC-QToF-MS using an Agilent 1200 Series system coupled to an AB Sciex Applied Biosystems mass spectrometer, operating in positive ion mode. A Zorbax Eclipse XDB C18 Solvent Saver Plus 3.5 μm (100 mm $\times$ 3.0 mm) column at 30 $^{\circ}\text{C}$ was utilized as stationary phase. The mobile phase was a mixture of two solutions, namely 0.1% formic acid in water (A) and 0.1% formic acid in methanol (B), in gradient mode. Solution A was injected at 95.0% during the first 10 min, 5.0% from 10 to 11 min, and 95.0% again until 15 min, at a flow rate of 0.6 $\text{cm}^3 \text{min}^{-1}$.

3. Results and discussion

3.1. Characterization of the ZnO/TiO₂/Ag₂Se thin films

The as-synthesized materials were analyzed by different physicochemical techniques. First, the crystal structure was ascertained by XRD. Fig. 2 presents the comparative XRD patterns recorded for the ZnO/TiO₂(3)/Ag₂Se(600), ZnO/TiO₂(3) and ZnO NRs thin films on FTO. In the three diffractograms, signals at 26.4°, 33.3°, 37.6°, 51.3°, 61.4° and 65.5° can be related to the tetragonal structure of SnO₂ from the substrate (JCPDS No. 41-1445). This was not due to uncoated areas, since this was discarded from other analyses discussed below, but to the small film thickness. Moreover, the three XRD patterns also show peaks at 31.7°, 34.3°, 36.2°, 47.5° and 62.8° corresponding to the (100), (002), (101), (102) and (103) planes, respectively, of the polycrystalline hexagonal wurtzite structure of ZnO NRs (JCPDS, No. 036-1451). The predominant signal of the (002) plane confirms the preferential vertical growth of the nanorods [54]. The diffractogram of ZnO/TiO₂(3) displays two additional signals at 25.5° and 63.3° assigned to the (101) and (204) planes, respectively, of anatase TiO₂ (JCPDS No. 21-1272), along with a peak at 39.1° related to the (200) plane of rutile TiO₂ (JCPDS No. 21-1276). This corroborates the effective coating of the underlying ZnO NRs matrix. The XRD pattern of ZnO/TiO₂(3)/Ag₂Se(600) reveals a peak at 34.8°, characteristic of the (121) plane of Ag₂Se (JCPDS No. 04-0783), that was almost overlapped with the strong ZnO signal at 34.3°. In addition, a very weak signal at 64.6° related to the (200) plane of residual Ag (JCPDS No. 04-0783), which is formed from reaction (5) and partially consumed from reaction (9), can be observed.

A comparative study between ZnO/TiO₂(3)/Ag₂Se(600) and an Ag₂Se(600) thin film onto FTO was additionally performed to confirm its formation upon the established procedure. Fig. S1 (curve *b*) evidences the existence of signals at 34.8°, 39.0° and 40.1° associated with the

(112), (013) and (122) planes of orthorhombic β -Ag₂Se (JCPDS No. 24-1041), along with a small signal at 64.6° related to Ag.

The components of the thin films were identified by Raman spectroscopy. Fig. S2a depicts the spectrum obtained for the ZnO NRs, which belongs to the spatial group C_{6v}^4 with theoretical phonons vibrational modes equal to $A_1 + 2B_1 + E_1 + 2E_2$ near the center of the Brillouin mode [55]. The band at 92 cm⁻¹ was associated to the E_2^{low} non-polar phonon, ascribed with the lattice vibration of the Zn atoms, whereas the E_2^{high} non-polar phonon related to the lattice vibration of the O atoms that characterizes the wurtzite phase of ZnO NRs appeared at 434 cm⁻¹. In contrast, the bands observed at 241, 554 and 627 cm⁻¹ corresponded to the B_1^{low} , B_1^{high} and $TA + B_1^{high}$ silent phonon modes due to the small dispersion along the Brillouin zone [55]. Fig. S2b (curve *a*) shows the Raman spectrum of the ZnO/TiO₂(3) thin film, where some vibrational modes of each component can be seen. Three bands at 322, 437 and 574 cm⁻¹ can be associated to the $E_2^{high} - E_2^{low}$ (from the sub-cells of the Zn and O atoms), E_2^{high} and B_1^{high} of the ZnO NRs, respectively. The other five bands are related to the anatase TiO₂ with $A_{1g} + 2B_{1g} + 3E_g$ active modes [56]. The most intense band at 145 cm⁻¹, along with those at 198 and 639 cm⁻¹, corresponded to the E_g mode, whereas the band at 397 cm⁻¹ was due to the B_{1g} mode and that of 516 cm⁻¹ to a doublet of the A_{1g} y B_{1g} modes. In the case of the ZnO/TiO₂(3)/Ag₂Se(600) thin film, the most relevant finding was the strong peak at 136 cm⁻¹ that can be observed in Fig. S2b (curve *b*), which was associated with the Ag-Se bond [57] and hence, confirmed the presence of Ag₂Se that was not so clear in the diffractogram of Fig. 2. The spectrum also highlights two much weaker bands at 390 and 630 cm⁻¹, related to the B_{1g} and E_g modes of TiO₂.

Fig. S3 shows the confocal 3D images recorded for ZnO NRs, Ag₂Se(600), ZnO/TiO₂(3) and ZnO/TiO₂(3)/Ag₂Se(600) films onto FTO. Their thickness was calculated through a Leica Map DCM 3D software from the 2D images selected from 10 points of each deposited layer.

The maximum and mean values obtained for the same point of the above thin films are illustrated in Fig. S4. Table 1 evidences that the final composite could be really considered a thin film, with a mean thickness of 1.19 μm . The greatest contribution was from the ZnO NRs, with a mean value of 0.85 μm . The three TiO_2 layers added a thickness of 0.19 μm , which was further increased upon Ag_2Se electrodepositions. These data were then used to determine the E_{gap} of the same thin films by UV/Vis DRS. The transmittance spectra of Fig. 3a show that the presence of Ag_2Se clearly improved the light absorption, especially within the visible spectral region. The E_{gap} of each thin film was obtained using the Tauc's method [58]. This procedure is based on the determination of the optical absorption coefficient (α) from Eq. (10), further used to solve the classical Eq. (11):

$$\alpha = -\frac{\ln T}{t} \quad (10)$$

$$\alpha h\nu = \alpha_0 (h\nu - E_{\text{gap}})^n \quad (11)$$

where T is the film transmittance, t is its mean thickness (given in Table 1) and n is a constant that depends on the probability of transition [58]. When the $(\alpha h\nu)^2$ vs energy plot is linear, it accounts for by the direct-allowed transition with $n = 1/2$ and extrapolation to zero value in y-axis (i.e., $\alpha = 0$) yields E_{gap} as the intercept. Fig. 3b shows the good linear fitting obtained for the four thin films. As can be seen, the $\text{Ag}_2\text{Se}(600)$ thin film presented the lowest $E_{\text{gap}} = 1.77$ eV, which slightly increased to 1.85 eV for $\text{ZnO}/\text{TiO}_2(3)/\text{Ag}_2\text{Se}(600)$. In contrast, the ZnO NRs and $\text{ZnO}/\text{TiO}_2(3)$ thin films had much greater E_{gap} values of 3.31 and 3.66 eV, respectively. Note that the bandgap energies of the composites agree quite well with the expected values of pure components, namely 1.8 eV for Ag_2Se , 3.4 eV for ZnO and 3.2 eV for TiO_2 [29,46]. This means that each layer maintains its optical characteristics and hence, decoration with Ag_2Se for 600s is a good method to ensure the photoactivity upon visible light irradiation.

The morphological characteristics of the thin films were then analyzed by FE-SEM. Fig. 4 depicts the images obtained for ZnO NRs at two different magnifications (images (a) and (b)), showing that the vertically-grown nanorods possessed hexagonal form. Their diameters were calculated using the Imagem software and through a lognormal fitting of the histogram, an average diameter of 55 nm was determined. The same average diameter of the nanorods was obtained in the ZnO/TiO₂(3) thin film, but with higher roughness due to the TiO₂ layers, as can be seen in the images (c) and (d) of Fig. 4. In the case of the ZnO/TiO₂(3)/Ag₂Se(600) thin film, the images (e) and (f) reveal that the Ag₂Se nanoparticles coated the surface of most nanorods with structures in rosette form. This is particularly evident on top of the rods, which show nanostructured caps, whereas along the rod walls the particles appeared as small protuberances. These findings corroborate the formation of excellent ZnO NRs, uniformly coated with TiO₂ and finally decorated with Ag₂Se nanoparticles.

The ZnO/TiO₂(3)/Ag₂Se(600) thin film was scratched in order to get a powder that was analyzed by HRTEM, and the images recorded at several magnifications are presented in Fig. 5. The nanorods had an average length of at least 500 nm, and the presence of many spherical particles attached to the walls, which could be plausibly related either to Ag or Ag₂Se, was evidenced (see image (b)). Fig. 6a depicts the EDX spectrum of the same thin film, confirming the presence of the elements Zn, Ti, O, Ag and Se. Fig. 6b shows the mapping of such elements at 400,000× in a selected scanning area. It can be seen that the most abundant elements along the nanorod were Zn, Ti and O, as expected from the presence of an underlying ZnO structure coated with TiO₂ films. In contrast, Ag was clearly concentrated on the side bright spots attached to the rod. Se atoms were not so abundant, but could be also associated to those same regions. This means that the final electrodeposition step promoted the decoration not only with Ag₂Se nanoparticles, but also with residual metallic Ag, thus confirming the signal identified in the diffractogram of Fig. 2.

The general XPS spectrum of the ZnO/TiO₂(3)/Ag₂Se(600) thin film is shown in Fig. 7a and the corresponding spectrum for each element is depicted in Fig. 7b-f. As can be seen in Fig. 7b, the characteristic peak of Zn 2p appeared at 1022.7 eV, in good agreement with the value of 1021.4 eV reported for ZnO NRs [59]. The Ti 2p signal highlighted in Fig. 7c corresponded to the oxidation state of Ti(IV) with binding energies of 459.5 and 465.2 eV, associated with the Ti 2p_{3/2} and Ti 2p_{1/2} states, close to previously reported values of 459.6 and 465.4 eV, respectively [60]. The deconvolution of the O 1s signal presented in Fig. 7d yielded three peaks at: (i) 530.7 eV, related to the O²⁻ of the Zn-O bond of ZnO NRs [60]; (ii) 531.3 eV, ascribed to the -OH group adsorbed at the oxide surface [60]; and (iii) 532.5 eV, due to the defects of O and surface OH of the oxide [61]. Fig. 7e shows that the Ag species presented two bands centered at 368.4 and 374.4 eV, related to the Ag 3d_{5/2} and Ag 3d_{3/2} orbitals, respectively [62], which were deconvoluted revealing the presence of the Ag-Se bond (367.9 and 374.0 eV), pure Ag (368.4 and 374.4 eV) and Ag⁺ ion (369.1 and 375.0 eV) [57,62,63]. The relative heights of these bands suggest the presence of more Ag₂Se than Ag⁺ ion at the surface of the ZnO/TiO₂(3) coating. No bands at 356.6 eV, typical of Ag₂O [57], was observed. Note that the presence of metallic Ag was also confirmed from the determined value of the modified Auger parameter, α [53]. Considering the AgM₄N₄₅N₄₅, AlK α and Ag 3d_{5/2} signals, α was 719.9 eV, which matched well with α = 720.2 eV for standard elemental Ag [64] and differed from the value reported for Ag₂Se [64]. On the other hand, the signal at 54.2 eV depicted in Fig. 7f was ascribed to Se 3d_{5/2}, which is in agreement with the presence of a selenide like Ag₂Se, different from 59.8 eV for SeO₂ and 55.9 eV for pure Se [53]. All these findings allow concluding that both, Ag₂Se and Ag nanoparticles decorated the ZnO/TiO₂ surface, but the absorption of visible light was ensured.

3.2. Photoelectrochemical degradation of oxytetracycline

A first set of PEC assays was carried out by treating 100 cm³ of 5 mg dm⁻³ OTC with 0.050 M Na₂SO₄ at natural pH 5.8 using different photoanodes, which were irradiated with a 36-W blue LED lamp and set at $E_{an} = +1.0$ V vs Ag|AgCl for 360 min. Worth noting, all the films showed a good recyclability, as revealed after more than 10 consecutive cycles without apparent loss of efficiency. No significant pH changes were observed during the runs.

Fig. 8a illustrates the decay of the normalized OTC concentration during the above assays. The quickest removal of the antibiotic was achieved using the ZnO/TiO₂(3)/Ag₂Se(600) thin film, yielding 96.5% of abatement at 360 min. Smaller concentration removals of 90.1% with ZnO/TiO₂(3)/Ag₂Se(900), 89.1% with ZnO/TiO₂(2)/Ag₂Se(900) and 84.2% with ZnO/TiO₂(2)/Ag₂Se(600) were found. This means that the photoanodes with three TiO₂ layers instead of two always performed better. This suggests that the global TiO₂ thickness played an important role to stabilize the photoanode, probably allowing a faster release of photogenerated e⁻_{CB} to the cathode that became beneficial to produce P([•]OH). For the best electrode, the shortest electrodeposition time for Ag₂Se was preferable, probably because longer times led to particle aggregation. The best photoanode, namely ZnO/TiO₂(3)/Ag₂Se(600), was then selected to carry out the subsequent assays. Fig. 8b highlights the excellent linear dependences obtained from the above concentration decays assuming a pseudo-first-order kinetics for OTC destruction. The corresponding apparent rate constants (k_1) are collected in Table 2. Good R -squared values ≥ 0.993 can be observed in all cases. The highest k_1 -value of $8.21 \times 10^{-3} \text{ min}^{-1}$ corresponded to the best photoanode, whereas the lowest rate constant of $5.05 \times 10^{-3} \text{ min}^{-1}$ was found for ZnO/TiO₂(2)/Ag₂Se(600). The observed kinetics for OTC abatement is indicative of the formation of a small and steady concentration of generated P([•]OH) oxidant, as well as the control of the process by OTC mass transport from the solution to the photoanode [10,29].

The efficiency of PEC process to degrade OTC was further compared with that of PC and EO processes, using the ZnO/TiO₂(3)/Ag₂Se(600) thin film either as photoanode, photocatalyst or anode, respectively. Fig. 8c depicts the poor oxidation ability of PC for the treatment of a 5 mg dm⁻³ antibiotic solution in sulfate medium at pH 5.8, only achieving 55.3% removal after 360 min of irradiation with of blue LED lamp. This means that a rather low quantity of P([•]OH) was produced from reaction (2) between water and h⁺_{VB} to destroy the antibiotic, because of the fast recombination of the photogenerated e⁻_{CB}/h⁺_{VB} pairs from reaction (3). The antibiotic concentration decreased much more rapidly in EO, with a final decay of 76.9%, suggesting a much greater formation of P([•]OH) by EO via reaction (4) than by PC via reaction (2). The hybrid PEC treatment outperformed the EO process since the combined use of the blue LED radiation and the current supply at $E_{an} = +1.0$ V vs Ag|AgCl allowed a much higher OTC removal (96.5%). In all these assays, the concentration decay always obeyed a pseudo-first-order kinetics, as expected if a steady and small content of the main oxidant P([•]OH) was formed in all cases, as stated above. The k_1 -values listed in Table 2 decreased in the order: PEC > EO > PC, in agreement with their oxidation ability. Note that the degradation achieved in PEC treatment was lower than the sum of that in PC and EO. For example, at 120 min of treatment, the concentration was reduced by 65.7% in PEC, whereas the independent sum of removals in PC and EO was 84.0%. This suggests an interference between the active sites that cause the photocatalysis (i.e., light absorption) and those that produce the anodic water oxidation, causing an efficiency loss.

Several comparative OTC degradation trials were carried out using a ZnO/Ag₂Se(600) photoanode, whose optical properties were analogous to those of ZnO/TiO₂(3)/Ag₂Se(600) (see Fig. 3b). The as-prepared photoanode performed well, yielding 95.4% of concentration decay after 360 min at +1.0 V vs Ag|AgCl (data not shown). However, the film was quite unstable, undergoing a marked photocorrosion that caused a strong loss of efficiency after 5

cycles. This phenomenon did not occur with the ZnO/TiO₂(3)/Ag₂Se(600) thin film, which could be recycled for more than 10 times, as stated above. According to FE-SEM, EDX and XPS analyses after these assays, the catalyst did not show any significant structural change (data not shown). As hypothesized in the Introduction, the intermediate TiO₂ layer turned out to be crucial to ensure the photoanode stability.

The degradation of the 5 mg dm⁻³ antibiotic solution in sulfate medium using the ZnO/TiO₂(3)/Ag₂Se(600) photoanode was performed at increasing bias potentials. Fig. 9a shows the profile of the normalized content vs time at $E_{an} = +1.2$ V vs Ag|AgCl. The higher quantities of P([•]OH) produced from reactions (2) and (4) upon a greater current supply as compared to the trial at $E_{an} = +1.0$ V vs Ag|AgCl yielded a much quicker OTC removal, being already degraded by 94.7% in 235 min with a 1.86-fold higher k_1 -value (see Fig. 9b and Table 2). Unfortunately, after 2 reuses at $E_{an} = +1.2$ V vs Ag|AgCl, the film underwent a strong corrosion and it was partly detached from the FTO substrate. This means that in order to ensure the long-term stability and reproducibility of the PEC treatment, E_{an} must be limited to +1.0 V vs Ag|AgCl as maximal. Other assays under these optimum conditions were made by using a 36-W UVA lamp instead of the visible light source, obtaining a similar OTC degradation (data not shown).

Finally, the effect of the aqueous matrix on the degradation ability of the best PEC system was investigated. To do this, 5 mg dm⁻³ of OTC were spiked into 100 cm³ of urban wastewater. In this medium, the degradation process is expected to be more complex due to: (i) the presence of NOM in the main form of fulvic and humic acids with a TOC of 9.1 mg C dm⁻³, which can partly consume the hydroxyl radicals [65], and (ii) the generation of active chlorine species such as HClO from oxidation of Cl⁻ present in the medium via reactions (12) and (13), which act as scavengers of P([•]OH) and attack the organics producing stable and toxic chloroderivatives [66,67].

Fig. 9a reveals a 91.0% removal in urban wastewater after 360 min at $E_{\text{an}} = +1.0$ V vs Ag|AgCl under visible light, a value slightly lower than 96.5% found in sulfate medium. This inhibition decreases the k_1 -value (see Fig. 9b and Table 2) and can be accounted for by the competitive oxidation of NOM, which was not counterbalanced by the simultaneous attack of $\text{P}(\bullet\text{OH})$ and HClO over the organics. These results allow concluding that ZnO/TiO₂(3)/Ag₂Se(600) thin films can successfully degrade OTC even in real water matrix without a substantial loss of performance.

3.3. Reaction by-products and proposed pathway

Samples at different electrolysis times were withdrawn from a 5 mg dm⁻³ antibiotic solution with 0.050 M Na₂SO₄ at natural pH treated by PEC using the ZnO/TiO₂(3)/Ag₂Se(600) photoanode at $E_{\text{an}} = +1.0$ V vs Ag|AgCl, and further analyzed by LC-QToF-MS. Five primary products were detected, allowing the proposal of the initial degradation pathway of OTC (**1**) presented in Fig. 10. The destruction of (**1**) occurred via four parallel routes involving: (i) demethylation in the C(6) position yielding compound **2**; (ii) dehydration in the C(5) and C(6) positions giving rise to compound **3**; (iii) hydroxylation of the phenolic ring, producing compound **4**; and (iv) ring cleavage at the C(1)-C(2) bond, with hydroxylation in each carbon position, leading to compound **5**. Compound **4** was subsequently transformed into **6** by demethylation of the amino group linked to its C(4) position. Note that products **2**, **3**, **4** and **6** have been previously reported for the PC treatment of OTC under different conditions [14,68,69]. Note that isomers of the proposed products could alternatively or complementarily be formed.

Fig. S5 shows the time course of OTC and its five primary products detected by LC-QToF-MS, along with their m/z and t_r values. As can be seen, most derivatives were rapidly

formed and completely destroyed before ending the PEC treatment. Only compound **2** was slowly accumulated until 60 min, whereupon it was slowly removed and still remained at 360 min of the assay. These findings confirm not only the oxidative disappearance of the target pollutant, but also of its by-products upon action of the generated $P(\bullet OH)$. Such parallel destruction routes decelerate the OTC removal, but ensure the gradual detoxification of solutions.

4. Conclusions

A photoanode composed of vertically grown ZnO NRs onto FTO, coated with 3 thin layers of anatase TiO_2 and subsequently decorated with Ag_2Se nanoparticles by electrodeposition for 600 s, was found optimal for OTC degradation by PEC. Its detailed characterization revealed the presence of hexagonal nanorods with a length greater than 500 nm, which became rougher upon TiO_2 deposition and had nanospherical Ag_2Se particles and residual Ag along the walls. The thin film had a mean thickness of 1.19 μm and $E_{gap} = 1.85$ eV, ensuring its photoactivity under visible light irradiation. A 96.5% of the antibiotic was removed after 360 min of electrolysis of a 5 $mg\ dm^{-3}$ solution with 0.050 M Na_2SO_4 at natural pH 5.8 using the $ZnO/TiO_2(3)/Ag_2Se(600)$ photoanode at $E_{an} = +1.0\ V$ vs $Ag|AgCl$. The electrode showed large recyclability thanks to photocorrosion minimization, provided by the presence of the TiO_2 protective layers on ZnO. PEC treatment outperformed PC and EO, thanks to the simultaneous photogeneration and electrogeneration of $P(\bullet OH)$ as main oxidant. In urban wastewater at near neutral pH, the antibiotic was degraded more slowly due to the partial destruction of radicals by NOM and active chlorine. The degradation pathways of OTC involved its demethylation, dehydration, ring opening and hydroxylation.

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Figure captions

Fig. 1. (a) Cyclic voltammogram recorded in a solution containing 0.10 mM $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.10 M NaNO_3 at 70 °C, using a 5 cm² FTO glass substrate as working electrode. Initial and final potential: 0.1 V; reversal potential: -1.3 V. (b) Consecutive cyclic voltammograms recorded on a 5 cm² $\text{ZnO}/\text{TiO}_2(3)$ coating on FTO, as working electrode, in a solution containing 0.50 M KSCN, 5.0 mM AgNO_3 , 2.5 mM H_2SeO_3 and 0.05 M KNO_3 at pH 3.0 and 25 °C. Initial and final potential: 0.8 V; reversal potential: -1.0 V. In both cases, the counter electrode was a Pt wire and the reference electrode was $\text{Ag}|\text{AgCl}$ (3 M KCl), and a scan rate of 50 mV s⁻¹ was employed. TiO_2 deposition on ZnO NRs was made via three coating cycles.

Fig. 2. XRD patterns of the synthesized (a) $\text{ZnO}/\text{TiO}_2(3)/\text{Ag}_2\text{Se}(600)$, (b) $\text{ZnO}/\text{TiO}_2(3)$ and (c) ZnO NRs thin films onto FTO. The crystallographic planes of each species, including TiO_2 anatase and rutile as well as residual Ag, are shown up. TiO_2 deposition on ZnO NRs was made via three coating cycles, whereas Ag_2Se deposition was performed at -0.65 V vs $\text{Ag}|\text{AgCl}$ for 600 s.

Fig. 3. (a) Transmittance spectrum and (b) Tauc plot for the thin films deposited onto FTO. TiO_2 deposition on ZnO NRs was made via three coating cycles, whereas Ag_2Se deposition was performed at -0.65 V vs $\text{Ag}|\text{AgCl}$ for 600 s.

Fig. 4. FE-SEM images recorded for (a,b) ZnO NRs, (c,d) $\text{ZnO}/\text{TiO}_2(3)$ and (e,f) $\text{ZnO}/\text{TiO}_2(3)/\text{Ag}_2\text{Se}(600)$ thin films onto FTO. Magnification: (c) 50,000×, (a,e) 100,000×, (d) 200,000× and (b,f) 400,000×.

Fig. 5. HRTEM images for the $\text{ZnO}/\text{TiO}_2(3)/\text{Ag}_2\text{Se}(600)$ thin film deposit onto FTO. Magnification: (a) 25,000× and (b,c,d) 100,000×.

Fig. 6. (a) EDX spectrum for the thin film of Fig. 5. (b) Elemental mapping at 400,000× showing the selected scanning area and the distribution of Zn, Ti, O, Ag and Se.

Fig. 7. (a) XPS spectrum for the thin film of Fig. 5. Spectra of the different elements present in the photoelectrocatalyst: (b) Zn 2p, (c) Ti 2p, (d) O 1s (deconvoluted), (e) Ag 3d (deconvoluted), and (f) Se 3d.

Fig. 8. (a) Normalized oxytetracycline concentration decay and pseudo-first-order kinetic analysis (inset) during the photoelectrocatalytic (PEC) treatment of 100 cm³ of solutions containing 5 mg dm⁻³ drug and 0.050 M Na₂SO₄ at pH 5.8 and 25 °C using a cell with different electrocatalysts, a Pt wire cathode and Ag|AgCl (3 M KCl) as the reference electrode. The solution was irradiated with a 36-W blue LED lamp and an anodic potential (E_{an}) of +1.0 V vs Ag|AgCl was applied. (b) Pseudo-first-order kinetic analysis for the above concentration decays. (c) Comparison between (□) photocatalysis (i.e., no current supply), (△) electrochemical oxidation (i.e., no light irradiation) and (▲) previous PEC.

Fig. 9. (a) Effect of experimental variables on the change of normalized drug concentration with electrolysis time for the PEC treatment of 100 cm³ of 5 mg dm⁻³ oxytetracycline solutions in 0.050 M Na₂SO₄ at pH 5.8 or urban wastewater at pH near 7 at 25 °C using a ZnO/TiO₂(3)/Ag₂Se(600) anode at several E_{an} and irradiated with a 36-W blue LED lamp. (b) Pseudo-first-order kinetic analysis for the above decays.

Fig. 10. Degradation pathways of oxytetracycline in sulfate medium by PEC using a ZnO/TiO₂/Ag₂Se thin film deposited onto FTO.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Table 1. Mean thickness of synthesized thin films onto FTO.

Thin film	Thickness (μm) ^c
ZnO NRs	0.85 ± 0.06
Ag ₂ Se(600) ^a	0.14 ± 0.13
ZnO/TiO ₂ (3) ^b	1.04 ± 0.15
ZnO/TiO ₂ (3)/Ag ₂ Se(600) ^{a,b}	1.19 ± 0.21

^a Ag₂Se deposition for 600 s

^b TiO₂ deposition via three coating cycles.

^c Average value of 20 measurements. Errors with 95% confidence level.

Table 2. Pseudo-first-order rate constant and the corresponding squared correlation coefficient for the decay of 5 mg dm⁻³ oxytetracycline in 100 cm³ solutions by different treatments under irradiation with a 36-W blue LED lamp.

Method	Medium	Anode	Anodic potential (V vs Ag AgCl)	k_1 (10 ⁻³ min ⁻¹)	R^2
PC ^a	0.050 M Na ₂ SO ₄	ZnO/TiO ₂ (3)/Ag ₂ Se(600)	-	3.63	0.981
EO ^b	0.050 M Na ₂ SO ₄	ZnO/TiO ₂ (3)/Ag ₂ Se(600)	+1.0	5.26	0.993
PEC ^c	0.050 M Na ₂ SO ₄	ZnO/TiO ₂ (2)/Ag ₂ Se(600)	+1.0	5.05	0.996
		ZnO/TiO ₂ (3)/Ag ₂ Se(600)	+1.0	8.21	0.998
		ZnO/TiO ₂ (3)/Ag ₂ Se(600)	+1.2	15.3	0.993
		ZnO/TiO ₂ (2)/Ag ₂ Se(900)	+1.0	6.49	0.995
		ZnO/TiO ₂ (3)/Ag ₂ Se(900)	+1.0	6.67	0.996
	Urban wastewater	ZnO/TiO ₂ (3)/Ag ₂ Se(600)	+1.0	6.73	0.987

^a Photocatalysis (without current supply).

^b Electrochemical oxidation (without light irradiation).

^c Photoelectrocatalysis.