



Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation

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ARTICLE INFO

Keywords:

2D TiO₂ nanosheets
Photocatalysis
Doping
g-C₃N₄
Carbamazepine
Acetaminophen
Pharmaceutical degradation
Photooxidation process

ABSTRACT

Novel photocatalysts of phosphorus and sulfur co-doped graphitic carbon nitride incorporated in 2D TiO₂ structure were successfully fabricated and applied for solar-driven degradation of emerging pollutants from the group of pharmaceuticals not susceptible to biodegradation. The hybrid photocatalysts with different loadings of (P, S)-doped g-C₃N₄ were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV–vis diffuse reflectance spectroscopy (DR/UV–vis), photoluminescence (PL) spectroscopy, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and transmission electron microscopy (TEM). The optimum (P, S)-doped g-C₃N₄/TiO₂ (5 %) composite revealed improved photocatalytic activity towards the degradation of carbamazepine and acetaminophen. For CBZ, about 100 % degradation was achieved in less than 30 min of photodegradation, whereas for ACT, the complete removal was observed in 60 min of irradiation under simulated solar light. The multi-anion doped g-C₃N₄/2D TiO₂ composite demonstrated an excellent synergy towards the degradation of CBZ and ACT with a synergy index of 1.35 and 1.62. Moreover, the mineralization efficiency measured as TOC removal was 76 % and 40 % for CBZ and ACT, respectively. The reactive oxygen species responsible for the degradation of selected pharmaceuticals are superoxide (O₂⁻) and hydroxyl radicals (HO[•]), and the kinetics of reactions proved to fit the first-order kinetics with a rate constant of 0.21 min⁻¹ for CBZ degradation and 0.074 min⁻¹ for ACT degradation. Our results suggest that (P, S)-doped g-C₃N₄/ 2D TiO₂ heterostructure is a Z-scheme heterojunction, which can effectively separate photogenerated charge carriers. The emissions and decay times analyzed for single components and the optimal (P, S)-doped g-C₃N₄/ 2D TiO₂ (5 %) composite confirmed interfacial charge transfer between TiO₂ nanosheets and (P, S)-g-C₃N₄ and more effective separation of electron-hole pairs. Identification of carbamazepine and acetaminophen intermediates was performed using LC-MS analysis in combination with additional DFT calculations of the possible by-products formation. Regarding reusability, the photocatalytic activity of (P, S)-doped g-C₃N₄/ 2D TiO₂ (5 %) was stable after subsequent cycles of carbamazepine and acetaminophen degradation.

1. Introduction

Water is a vital resource for natural ecosystems and human life. Therefore, assuring a high quality of water and protecting it from contamination is one of the critical goals of sustainable development in the contemporary world. In recent years, pharmaceutically active compounds and personal care products have become a class of emerging environmental contaminants that are extensively and increasingly being

detected in aquatic systems [1–3]. Some of the commonly and worldwide used non-steroidal anti-inflammatory drugs such as ibuprofen, diclofenac, ketoprofen, naproxen and acetaminophen are not susceptible to biological degradation, therefore passing through a cycle of biological treatment in the unchanged form being detected in trace amounts in surface waters, maritime and wastewater treatment plants [4–6]. Among them, acetaminophen (ACT), also commonly known as paracetamol, is a pharmaceutical agent consumed abundantly and

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<https://doi.org/10.1016/j.seppur.2023.123320>

Received 19 December 2022; Received in revised form 21 January 2023; Accepted 28 January 2023

Available online 1 February 2023

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possesses a highly stable nature, making its degradation with conventional water treatment technologies limited. Acetaminophen can cause cardiovascular, gastrointestinal, kidney diseases, and its metabolites may induce mutagenic effects in human cells [7]. Carbamazepine - dibenzazepine derivative with antiepileptic and psychotropic activity is also well established in treating severe pain syndromes associated with neurological disorders, such as trigeminal neuralgia. Carbamazepine shows low sorption properties and high persistence to biodegradation [8]. Both pharmaceuticals are examples of active pharmaceutical ingredients frequently detected in WWTP effluents, surface waters, groundwater, and occasionally in drinking water in Europe, America, and Asia [9,10]. Furthermore, these pharmaceuticals may have chronic and synergistic ecotoxicological effect in the mixture with other non-steroidal anti-inflammatory drugs [11,12]. Regarding the toxic effects, including bioaccumulation, the most important requirement is the removal of this drugs residues from aquatic systems.

Commonly used methods, including biodegradation [10], chemical oxidation in the presence of persulfate [13], or chlorine [14], are still far from satisfactory concerning the removal of carbamazepine and can generate toxic chlorinated by-products, such as trichloroacetic acid, dichloroacetonitrile, and trichloronitromethane [15].

Recently, advanced oxidation processes (AOPs), including photocatalysis, ozone-based processes such as O_3/H_2O_2 or O_3/UV systems, and Fenton/Fenton-like reactions, are considered the most effective technologies for the treatment of waters containing trace amounts of pharmaceutical pollutants. AOPs are based on the chemistry of hydroxyl radicals (OH \cdot), which are non-selective reactive species able to oxidize persistent organic pollutants into non-toxic susceptible to biodegradation intermediates or mineral end-products, yielding CO_2 and inorganic ions [16]. De Luna et al. [17] reported the degradation of acetaminophen by Fenton oxidation in the presence of high concentrations of H_2O_2 and Fe^{2+} . The reaction mixture containing Fe^{2+} ions as catalyst showed 100 % degradation in less than 40 min of process. Furthermore, Fenton-like oxidation is reported as an effective method for CBZ degradation in aqueous solutions under simple operational conditions and within a short time [18]. However, the main drawbacks are the strong acid environment (pH of 3–4) required for the best performance, the relatively high cost of reagents consumption, and the production of ferric sludge [18,19]. Ozone-based processes are capable of the efficient removal of pharmaceuticals [20]. However, they may generate toxicity due to detrimental degradation by-products formation caused by incomplete mineralization. Moreover, the operational costs are often relatively high due to high energy and chemical consumption [16,21].

Among the advanced oxidation processes, heterogeneous photocatalytic oxidation of persistent organic pollutants is considered a sustainable water purification technique since many recalcitrant organic compounds at low concentrations can be oxidized at room temperature in the presence of a semiconductor photocatalyst. At present, the need to develop green, solar-induced chemical processes, such as photocatalysis, is limited by low photoactivity under UV-vis (solar) light, reduced quantum efficiency, and a high recombination rate of photogenerated charge carriers [22,23]. Different types of photocatalysts have been reported to successfully degrade the contaminant molecules from the aqueous phase. Titanium(IV) oxide is widely used in photocatalytic processes due to its chemical and physical stability, low cost, and strong oxidizing properties. Despite the numerous advantages, TiO_2 can be activated almost only by ultraviolet light due to its wide bandgap of about 3.2 (eV).

In order to enhance the performance of semiconductor nanostructures, a suitable architecture, which integrates the usually incompatible features of large specific surface area, high charge-carrier mobility, low electron-hole recombination rate, is highly demanded. In view of this, ultrathin 2D TiO_2 is a promising photocatalytic material that provides many active sites for photocatalytic reactions, allowing the facile adhesion of organic molecules and improved functionality [24,25]. Furthermore, TiO_2 nanosheets minimize the diffusion distance,

which photoinduced electron-hole pairs overcome before reaching the solid-water interface, providing a charge transport pathway. Despite the 2D nanosheet structures offer much improvement in the photocatalytic process compared to the bulk 3D TiO_2 crystals, the quantum size effects within the small thickness of the TiO_2 nanosheets may lead to lowering the crystallinity and enlarging the E_g value. Overcoming the limitations related to the reduced spectral activation and recombination between photogenerated electrons and holes, which is often the largest hindrance in photocatalytic efficiency, the aim of the present study was the preparation of 2D TiO_2 -based hybrid photocatalyst with improved photocatalytic activity by heterojunction nanolayered TiO_2 with other electron donor semiconductor material.

Recently, 2D graphene-based materials have attracted much attention as an additive photocatalyst for solar light-driven photodegradation of organic pollutants. For example, graphitic carbon nitride ($g-C_3N_4$) has great potential to work as an efficient, multifunctional material with a medium bandgap of 2.7 (eV), high stability, and photocatalytic activity in the visible light range [26]. Cao et al. [27] reported that nitrogen vacancies graphitic carbon nitride (NV- $g-C_3N_4$) enhanced the photodegradation efficiency of CBZ since N-vacancies served as electron traps, thus hindering electron-hole recombination. Tubular graphitic carbon nitride ($g-C_3N_4$) modified with carbon quantum dots (CQD) effectively improved the CBZ photodegradation due to the hindrance effect of CQD in the e^- - h^+ recombination [28]. A photocatalyst configuration of TiO_2 /graphene/ $g-C_3N_4$ was demonstrated to significantly degrade acetaminophen under simulated solar light irradiation using hydroxyl radicals (HO \cdot) and superoxide radicals ($O_2^{\cdot-}$) as oxidizing species. After 120 min of irradiation, 100 % of ACT was degraded, and TOC removal was above 70 % [29]. Combining $g-C_3N_4$ with inorganic semiconductor such as TiO_2 significantly decreases the recombination rate of electrons and holes [26,30]. Moreover, the heterojunction between $g-C_3N_4$ and TiO_2 increases the composite interfacial contact area, making more efficient charge transfer at the interface [30]. Zhou et al. [31] reported that a Z scheme 2D nanosheet/nanotube $g-C_3N_4/TiO_2$ demonstrated high performance in the degradation of rhodamine B (RhB) and tetracycline hydrochloride under visible light range. Furthermore, in the study performed by Chen and co-workers, 3D $g-C_3N_4/TiO_2$ photocatalyst degraded 87 % of ibuprofen (5 mg/L) from the model solution within 60 min in the presence of visible light irradiation [32]. Besides, the combination of $g-C_3N_4/TiO_2$ with different chemical elements is reported to improve the photocatalytic activity of heterocomposite. Non-metal doping elements (C, B) [33], (C, N) [34], (P, O)[35], and (N, S) [36] have been reported to improve the photocatalytic activity of $g-C_3N_4/TiO_2$ according to applications in water splitting and photodegradation of methylene blue (MB), enrofloxacin, rhodamine B (RhB) and Cr(VI) reduction.

In the present study, the 2D TiO_2 -based hybrid photocatalysts were prepared for the first time by heterojunction of layered TiO_2 obtained by fluorine-free lyophilization method and modified with multi-anion doped $g-C_3N_4$. The as-obtained anatase nanosheets were used as building blocks for hybridization with graphitic carbon nitride to enhance photocatalyst performance. Furthermore, to improve the properties of the 2D $TiO_2/g-C_3N_4$ composite, precursors of phosphorus and sulphur were introduced into the structure of $g-C_3N_4$. The addition of sulfur in the $g-C_3N_4$ increased the porosity of the surface since it homogeneously substitutes the lattice nitrogen (N), while the addition of phosphorus (P) increased the separation efficiency of photogenerated electrons and holes and decreased the energy bandgap of semiconductor [37,38]. Even though research studies have been reported on the separate use of phosphorus and sulfur for improving the photocatalytic activity of carbon nitride-based photocatalyst and TiO_2 , no studies have focused on the synthesis and application of 2D TiO_2 modified with co-doped (P, S)- $g-C_3N_4$.

The (P, S)-doped $g-C_3N_4$ combined with 2D TiO_2 with a mass ratio of (P, S)- $g-C_3N_4$ to 2D TiO_2 of 2.5, 5, 10, and 20 wt% were applied for carbamazepine and acetaminophen photocatalytic degradation under

simulated solar light. The reaction kinetics and the reusability of the prepared photocatalysts were also investigated, and possible mechanisms and photodegradation pathways of carbamazepine (CBZ) and acetaminophen (ACT) were proposed according to identified intermediates and DFT calculations.

2. Experimental

2.1. Materials

In this study, thiourea (99 %), melamine (99 %), diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ (≥ 98 %), and titanium oxysulfate (≥ 29 % Ti as TiO_2 , basis, technical) were purchased from Sigma Aldrich. Ammonia solution (25 %), hydrogen peroxide H_2O_2 (30 %), and methanol were obtained from (POCH S.A.). The selected organic pollutant of carbamazepine and acetaminophen (99 % pure Bio extra) were purchased from Sigma Aldrich. The anionic surfactant of sodium dodecyl sulfate (SDS; 85 % pure) was purchased from (ACROS-Organics). The scavengers of ammonium oxalate, para benzoquinone (P-BQ), sodium azide (NaN_3), silver nitrate (AgNO_3), and isopropanol were provided from Sigma Aldrich and used without any further purification. HPLC gradient grade, acetonitrile, and orthophosphoric acid were provided by Merck.

2.2. Synthesis of (P, S) co-doped g- C_3N_4

Phosphorus and sulfur co-doped graphitic carbon nitride was obtained by thermal treatment. In this regard, 7.5 g thiourea, 7.5 g melamine, and 1.36 g $(\text{NH}_4)_2\text{HPO}_4$ were mixed and grounded to form a powder. The obtained powder was heated at 550°C for 4 h with a rate of $2^\circ\text{C}\cdot\text{min}^{-1}$. Calcination enables the linkage of P and S atoms in the g- C_3N_4 network. After thermal treatment, the obtained agglomerates were grounded into a powder and heated at 500°C for 3 h, with a rate of $5^\circ\text{C}\cdot\text{min}^{-1}$. The final obtained product was a fine light yellow powder of (P, S)-doped g- C_3N_4 .

2.3. Synthesis of 2D TiO_2 nanosheets

The TiO_2 nanosheets were prepared using the freeze-drying method as a green concept for the synthesis. Titanium oxysulfate (10 g) was dissolved in 300 cm^3 of deionized water at 40°C . Then, the solution was cooled down until it reached 5°C and the ammonia solution was added dropwise until a pH of 9. The obtained white precipitate was centrifugated, washed, and re-suspended in 300 cm^3 of deionized water. Furthermore, 60 cm^3 of 30 % aqueous H_2O_2 was added to the suspension, the suspension turned yellow, and the pH dropped to 2. The solution was aged at 5°C to form a gel, and then it was frozen using liquid N_2 . Further, the sample was placed into a freeze-dryer and lyophilized. In the last step, the dry powder was calcinated at 700°C to form the final TiO_2 nanosheets.

2.4. Synthesis of (P, S) co-doped g- $\text{C}_3\text{N}_4/\text{TiO}_2$

The (P, S) co-doped g- C_3N_4 was coupled with 2D TiO_2 in 50 cm^3 of methanol in the presence of an anionic surfactant, SDS (sodium dodecyl sulfate salt, 2 % w/w). The mixture was sonicated for 30 min. Finally, the suspension was washed 3 times with deionized water and dried in the oven at 100°C for 4 h. Four different types of composite with different mass ratios of (P, S) co-doped g- C_3N_4 (2.5; 5; 10 and 20 % w/w) to 2D TiO_2 were prepared.

2.5. Characterization of photocatalysts

The phase composition of prepared photocatalysts was analyzed using X-ray powder diffraction (Cu $\text{K}\alpha$ radiation, Rigaku MiniFlex 600 X-ray diffractometer). Data samples were measured in the 2θ range 5 – 80°

with a scan speed of $1^\circ/\text{min}$ and scan step of 0.01° . The analyses were performed based on the International Centre for Diffraction Data (ICDD) database. Debye-Scherrer equation was used to estimate the particle size of the photocatalyst, and it consists of the following $D = K\lambda/\beta\cos\theta$, where K stands for Scherrer constant, λ presents the wavelength of the X-ray beam, β is the full width at half maximum of the peak, and lastly, the Bragg angle is represented by theta (θ).

The Brunauer-Emmett-Teller (BET) surface area of the photocatalysts was investigated using Micromeritics Gemini V (model 2365) (Norcross, GA, USA). Before performing nitrogen adsorption measurements, the prepared samples were degassed at 200°C for 2 h. The diffuse reflectance (DR) spectra were measured by UV-vis spectrophotometer (Thermo Fisher Scientific Evolution 220) using BaSO_4 as a standard. The bandgap energy was calculated using the Kubelka-Munk function.

Microscopic measurements were performed using scanning electron microscope (Quanta 3D FEG, FEI Europe) with secondary electron (SE) detector (Everhart-Thornley detector) and transmission electron microscope (model Tecnai F20 X-Twin) coupled with the spectroscopic techniques (EDS, EELS). In TEM mode, a dark field (DF) detector was used for imaging. In the STEM mode, a high angle annular dark field (HAADF) detector was used for imaging, and energy dispersive spectrometer (EDS) RTEM SN9577+, by EDAX (Pleasanton, USA), or parallel electron energy loss spectroscopy (PEELS) by Gatan (Pleasanton, USA) was used to analyze the elements.

The chemical states on the surface of photocatalysts were examined by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopic (XPS) measurements were performed using a PHI 5000 VersaProbe (ULVAC-PHI) spectrometer with monochromatic Al $\text{K}\alpha$ radiation ($h\nu = 1486.6\text{ eV}$) from an X-ray source operating at $100\text{ }\mu\text{m}$ spot size, 25 W and 15 kV. The high-resolution (HR) XPS spectra were collected with the hemispherical analyzer at the pass energy of 117.4 and the energy step size of 0.1 eV. The X-ray beam was incident at the sample surface at the angle of 45° with respect to the surface normal, and the analyzer axis was located at 45° concerning the surface. The CasaXPS software was used to evaluate the XPS data. Deconvolution of all HR XPS spectra was performed using a Shirley background and a Gaussian peak shape with 30 % Lorentzian character.

The Fourier Transformer Infrared Spectroscopy (FTIR) measurements were performed using a Nicolet iS10 FTIR spectrometer in the scan range of 400 – 4000 cm^{-1} as the diffuse reflectance for powder samples in KBr with the resolution of 2 cm^{-1} .

The zeta potential analyses were performed using Nano-ZS Zetasizer dynamic light scattering detector (Malvern Instruments UK) equipped with a 4.0 mW internal laser.

X-ray fluorescence spectroscopy (XRF) using a WDXRF S8 TIGER analyzer (Bruker, S8 TIGER, Bruker, Karlsruhe, Germany) was employed to evaluate the sulfur content in (P, S)-g- C_3N_4 . The analyses were performed according to the standard PN-EN 15309:2010.

Diffuse reflectance spectra (DR/UV-vis) in the 200 – 800 nm range were recorded and converted to absorption using ThermoScientific Evolution 220 Spectrophotometer (Waltham, MA, USA) equipped with PIN-757 integrating sphere. The optical bandgap of 2D TiO_2 and 2D $\text{TiO}_2/\text{g-}\text{C}_3\text{N}_4$ composites were calculated from the Kubelka-Munk function of $\alpha h\nu = A(h\nu - E_g)^n$, where α is the absorption coefficient, $h\nu$ is the photon energy (eV), h is Planck constant, ν is the frequency (s^{-1}), A is a constant, n is equal to 0.5.

The Raman spectra of the photocatalysts were investigated using the Renishaw InVia Raman spectrometer equipped with an IR laser diode and a CCD camera as a detector. The polarized Raman spectra were excited with the IR diode laser emitting at 830 nm (1 mW) and recorded in a single scan with a 30 s exposure time using a $20\times$ LWD objective.

Emissions and decay times measurements were performed using an excitation source consisting of a femtosecond laser (Coherent Model "Libra") coupled to the optical parametric amplifier (Light Conversion Model "OPERA"). The system delivers 100 fs pulses at a repetition rate regulated up to 1 kHz at a wavelength tuned between 230 and 2800 nm.

The luminescence spectra and decay curves were recorded with a grating spectrograph (Princeton Instr. Model Acton 2500i) coupled to a streak camera (Hamamatsu Model C5680) with a temporal resolution of 20 ps.

The Mott-Schottky analysis was performed to determine the flat band (F_b) potential of the photocatalyst. The EIS data were recorded from the anodic towards a cathodic direction using Potentiostat/Galvanostat Autolab PGSTAT204 (Metrohm Autolab) with a Na_2SO_4 (0.5 M) as an electrolyte. EIS data were recorded for the applied frequency of 1000 Hz in the potential range from + 1.0 to - 1.5 V vs. Ag/AgCl. The spectra were run at the frequency range from 20 kHz to 0.1 Hz with a 10 mV amplitude of the alternating current.

The photon flux measurements were performed by UV-vis spectrophotometer (Thermo Fisher Scientific Evolution 220) using BaSO_4 as a standard. The wavelength range of 300–400 nm was used to record the absorption spectra for 2D TiO_2 and (P, S)-g- C_3N_4 /2D TiO_2 (5 %). Optical properties of the best-performing sample (5 % composite) in comparison to the pure 2D TiO_2 , following the procedures reported in the literature [39].

2.6. Photocatalytic degradation

The photocatalytic activity was evaluated by the degradation of carbamazepine (CBZ; 14 $\text{mg}\cdot\text{dm}^{-3}$) and acetaminophen (ACT; 20 $\text{mg}\cdot\text{dm}^{-3}$). Photocatalytic activity for the prepared samples was measured using a photocatalytic set-up in a black box. The pharmaceutical solution was stirred for 30 min in the dark to ensure the equilibrium of adsorption-desorption. After 30 min, the UV-vis irradiation (xenon lamp, 30 $\text{mW}\cdot\text{cm}^{-2}$) was introduced into the reactor. The samples were collected within the time frame of -30, 0, 15, 30, 60, and 120 min. Quenching experiments were performed to identify the main active species in the photocatalytic process. In this regard, 1 mM of isopropanol ($\cdot\text{OH}$ scavenger), ammonium oxalate (h^+ scavenger), benzoquinone BQ (O_2^- scavenger), sodium azide ($^1\text{O}_2$ scavenger), and silver nitrate (e^- scavenger) was added in the reaction solution of selected pharmaceutical. Photodegradation efficiency was monitored using a high-performance liquid chromatography system (HPLC, model Shimadzu LC-6A) equipped with a photodiode array detector (SPD-M20A) and C18 column (Phenomenex Gemini 5 μm ; 150 \times 4.6 mm) working at 45 $^\circ\text{C}$. For HPLC measurements of carbamazepine (CBZ), the mobile phase consisted of (v/v) 60 % H_2O , 0.5 % orthophosphoric acid (85 % w/v solution), and 39.5 % acetonitrile was used at a flow rate of 1.5 $\text{cm}^3\cdot\text{min}^{-1}$. On the other hand, the mobile phase for ACT consisted of (v/

v) 30 % methanol (MeOH), 69.9 % H_2O , and 0.1 % formic acid (HCOOH) with a flow rate of 0.8 $\text{cm}^3\cdot\text{min}^{-1}$.

The synergy values were calculated to evaluate whether the heterocomposite formation is efficient in the degradation of CBZ and ACT, as compared to the semiconductors separately. Additionally, these values can provide the information regarding which of formed heterocomposites demonstrates greater efficiency. Synergy coefficients were calculated accordingly to the given formula: $S = \frac{k(\text{heterocomposite})}{k(\text{P,S-g-C}_3\text{N}_4) + k(2\text{DTiO}_2)}$, where k (min^{-1}) is the rate constant obtained for degradation of pharmaceutical in the presence of heterocomposite, and rate constants obtained for degradation of pharmaceutical for semiconductors separately.

Additionally, the mineralization efficiency of CBZ and ACT was studied as total organic carbon (TOC) removal using the Shimadzu TOC-L apparatus. Quantitative analyzes were performed using the external calibration method with a standard compound obtained by Sigma-Aldrich.

Optical properties of the photocatalyst suspensions were determined for the best-performing composite and 2D TiO_2 as a control to check for possible differences in the photon-absorption ability of both materials. Experimental determination of the mass-specific extinction/absorption coefficients was based on the absorbance values obtained from direct/scattered transmittance measurements through the suspensions with different powder concentrations [39]. Measurements were performed in the wavelength range of 300–400 nm, and final values were obtained as an average value in this region. Obtained optical parameters of both samples were used to numerically model the local volume rate of photon absorption (LVRPA), following the six-flux model approach [40]. Detailed calculations followed the procedure reported by Acosta-Herazo et al. [41]. The applied scattering probabilities in the forward, backward and side directions were 0.754, 0.133 and 0.028, respectively, following the Henyey-Greenstein phase function, as suggested for the TiO_2 materials [41]. Integration of the LVRPA over the cross-section of the reactor was performed to calculate the total rate of photon absorption (TRPA) for a unit length of the reactor. A comparison of the TRPA value with the incident photon flux was used to estimate the total number of absorbed UVA photons during the process for both materials.

Identification of intermediates was performed using the high-performance LC-MS system, which consisted of an HCT Ultra spectrometer (Bruker Daltonics, Billerica, Massachusetts, US) with an ESI source coupled with an Agilent 1200 liquid chromatograph (Agilent Technologies, Santa Clara, California, US). Chromatographic separation was conducted on Eclipse XDB-C8, 4.6 \times 150 mm, 5 μm (Agilent) column. Mobile phase A was water with 0.1 % formic acid and phase B acetonitrile with 0.1 % formic acid. Gradient program was as follows: 0 min - 1 % B, 5 min - 1 % B, 25 min - 90 % B, 30 min - 90 % B, 35 min - 1 % B. The flow was set at 0.4 ml/min, and the injection volume was 50 μl . Column oven temperature was set to 25 $^\circ\text{C}$ and UV chromatograms were recorded at: 220, 246 and 254 nm. Spectra were acquired in positive and negative ESI mode, the capillary voltage was set at 113 V, the scanned mass range was 50–850 m/z and the accumulation time was 200,000 ms. The parameters capillary voltage, drying gas flow, nebulizing gas and source temperature was respectively: 4.0 kV, 10 L min $^{-1}$, 30 psi and 350 $^\circ\text{C}$. Helium (99.999 %) was used as the collision gas in the ion trap. The mass spectrometer was operated in full scan and single ion monitoring modes (SIM).

2.7. Computational analysis of degradation products

Computational analysis of the possible degradation by-products was performed at the density functional theory level (DFT) using Orca 5.0.3 software package [42]. All considered structures were modeled using B3LYP functionals [43] with the aug-cc-PVDZ basis set and included the conductor-like polarizable continuum model (CPCM) to account for the water matrix effect. The geometry of each compound was optimized to the default convergence thresholds of energy, gradient, and

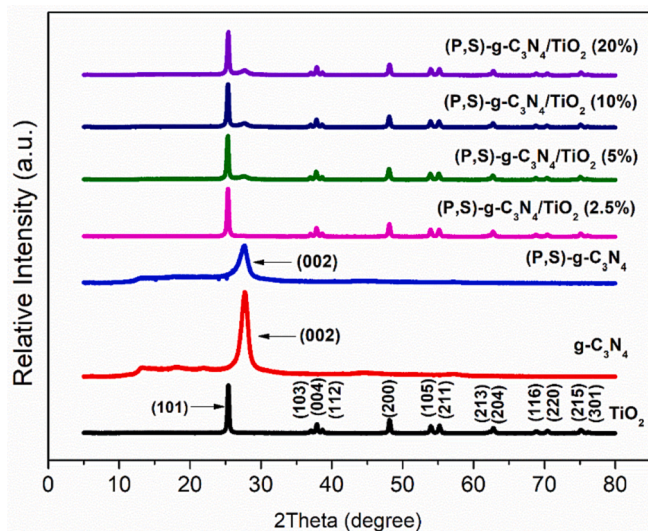


Fig. 1. XRD diffraction patterns of prepared photocatalysts.

Table 1

Characterization of the obtained photocatalysts. The surface area, pore volume and bandgap energy.

Photocatalyst	Surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Band gap energy (eV)
2D TiO_2	10.98	0.018	3.15
$\text{g-C}_3\text{N}_4$	16.56	0.0084	2.60
(P, S)- $\text{g-C}_3\text{N}_4$	17.41	0.0084	2.42
(P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (2.5 %)	17.58	0.0087	3.00
(P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %)	17.97	0.0087	2.90
(P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (10 %)	17.29	0.0086	2.85
(P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (20 %)	17.27	0.0086	2.85

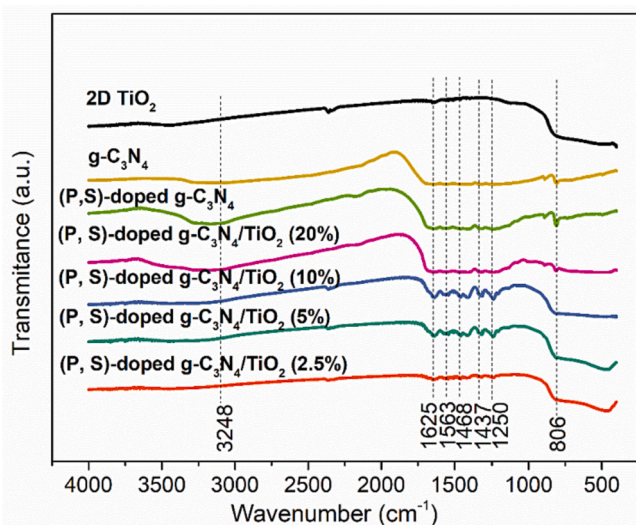


Fig. 2. The FTIR spectra for the obtained photocatalysts.

displacement. The energy effect of the possible reaction was calculated as the products-substrates energy difference, using O_2 and H_2O molecules to balance the stoichiometry (during the photocatalytic process, a number of reactive oxygen species are expected to form and react with pollutant, however O_2 and H_2O are both primary substrates, as well as final re-created products in the ambient conditions after the process). For the selected compounds, additional time-dependent DFT calculations were performed at the optimized geometry to simulate expected absorption spectra. Moreover, in the case of two carbamazepine structures, possible rearrangement of the molecule was studied using nudged elastic band method to determine the possible energy barrier and transition state of such a process. Finally, calculations of Fukui functions were performed based on the electron density maps for neutral, $N + 1$ and $N - 1$ electron states (N is a number of electrons) of the acetaminophen dimer to possibly suggest positions of the further reactive species attack.

3. Results and discussion

3.1. Characterization of obtained photocatalysts

The results of X-ray diffraction (XRD) analysis of 2D TiO_2 , (P, S)-doped $\text{g-C}_3\text{N}_4$, and (P, S)-doped $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composite are presented in Fig. 1. The 2D TiO_2 photocatalyst exhibited characteristic peaks indexed to the corresponding anatase phase planes (JCPDS 21-1272). The most intensive peak of the (101) diffraction plane of TiO_2 at $25.53^\circ 2\theta$ was noticed for 2D TiO_2 and all obtained (P, S)-doped $\text{g-C}_3\text{N}_4/$

TiO_2 composites. The distinct peak at $27.71^\circ 2\theta$ with the corresponding (002) diffraction plane of graphitic carbon nitride is ascribed to the interlayer stacking structure of the aromatic compound, and a signal at $13.21^\circ 2\theta$ with (100) plane is attributed to the in-plane repeat motif of tri-s-triazine [44]. The diffraction plane (100) at $13.21^\circ 2\theta$ was observed only for the $\text{g-C}_3\text{N}_4$ sample and started to vanish in the composites indicating the complete unification of both phases. Identified diffraction peaks of both (P, S)-doped $\text{g-C}_3\text{N}_4$ and 2D TiO_2 are observed in all samples of (P, S)-doped $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites, except (P, S)-doped $\text{C}_3\text{N}_4/\text{TiO}_2$ (2.5 %), where the peak was not detectable, but the presence of (P, S)-doped $\text{g-C}_3\text{N}_4$ was later confirmed by FT-IR analysis. The crystallite size of (P, S)-doped $\text{g-C}_3\text{N}_4$ was 15 nm, and 2D TiO_2 was about 33 nm.

Furthermore, the surface area of doped graphitic carbon nitride and 2D TiO_2 was found to be $17.41 \text{ m}^2 \cdot \text{g}^{-1}$ and $10.98 \text{ m}^2 \cdot \text{g}^{-1}$ (see Table 1). The composites of (P, S)-doped $\text{g-C}_3\text{N}_4/\text{TiO}_2$ possessed a surface area of about $17\text{--}18 \text{ m}^2 \cdot \text{g}^{-1}$ similar to that of (P, S)- $\text{g-C}_3\text{N}_4$. Furthermore, the pore volume for 2D TiO_2 was about $0.018 \text{ cm}^3 \cdot \text{g}^{-1}$, and the pore volume for (P, S)- $\text{g-C}_3\text{N}_4$ was $0.0087 \text{ cm}^3 \cdot \text{g}^{-1}$. The pore volume of composites was comparable to that of (P, S)-doped $\text{g-C}_3\text{N}_4$.

Three different bands can be distinguished at FTIR spectra of $\text{g-C}_3\text{N}_4$ and (P, S)-doped $\text{g-C}_3\text{N}_4$, as presented in Fig. 2. The broad peak at 3248 cm^{-1} is attributed to the stretching vibrations of the N—H group. The stretching and rotation vibrations of C—N and C=N of $\text{g-C}_3\text{N}_4$ were detected in the region of $1250\text{--}1625 \text{ cm}^{-1}$, whereas s-triazine ring vibrations are observed at 806 cm^{-1} [45]. For the 2D TiO_2 sample, the broad band between 500 and 750 cm^{-1} is ascribed to the stretching mode of the Ti—O—Ti bridge [32]. The characteristic range band between 1250 and 1625 cm^{-1} is noticed for all composite samples, indicating thus the presence of (P, S)-doped $\text{g-C}_3\text{N}_4$ at the surface of 2D TiO_2 . Furthermore, the presence of (P, S) was proved through XPS and XRF analyses.

The structure of photocatalysts was further characterized by microscopy analyses, and the results are presented in Fig. 3. The SEM images showed the platelet-shaped of (P, S)- $\text{g-C}_3\text{N}_4$ and 2D planar nanosheets of anatase (Fig. 3 a-b). The TEM microscopic analyzes confirmed the formation of the 2D TiO_2 structure of anatase (Fig. 3d). The FFT analysis of the noise-refined TEM lattice fringe images (Fig. 3e) revealed lattice spacing values of 0.19 nm , 0.235 nm , 0.368 nm , 0.349 nm , which are in good agreement with the crystal plane spacing $d(\text{hkl})$ of (200), (001), (010), (101) of anatase, respectively, thus indicating that the zone axis is [001] [46,47]. In Fig. 3 f-g, magnification of (P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) obtained from melamine as a precursor showed that (P, S)- $\text{g-C}_3\text{N}_4$ platelet-like particles are almost homogeneously well dispersed throughout the structure of anatase nanosheets. According to previous studies, the precursor used for the synthesis of carbon nitride ($\text{g-C}_3\text{N}_4$) is responsible for the morphology of produced photocatalyst. It has been reported that thiourea and urea mainly give exfoliated thin and thick planar sheets, while implementation of cyanamide and melamine precursors manifests into platelet-like shape particles and planar sheet-type morphology [48]. Furthermore, the EDX elemental composition analysis confirmed the successful doping of (P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) heterocomposite with P atoms. The lack of S atoms is due to the small amounts of S in the composition, but the presence of sulfur atoms in the lattice of nanocrystals was further proved by XPS and XRF analyses. Additionally, particle size distribution analysis showed the majority of nanoparticles in the range of $35\text{--}42 \text{ nm}$ (Fig. 3g).

The survey XPS spectra of 2D TiO_2 and 2D TiO_2 -based composites containing from 2.5 % to 10 % of (P, S)-doped $\text{g-C}_3\text{N}_4$ recorded in the binding energy (BE) range of 0 to 1300 eV are presented in Figure S1 in the Supporting Material. The peaks were identified in the same positions for all the composite materials. The only difference is the third identified chemical bond in N 1s spectra, where instead of NO_2 , it was shown to be C-NH₂ at the position of 401.99 eV . Related to the slight shifts of peaks, it can be explained by the differences in the content of (P, S)-doped $\text{g-C}_3\text{N}_4$ in the composites of (P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (2.5 %), (P, S)- $\text{g-C}_3\text{N}_4/$

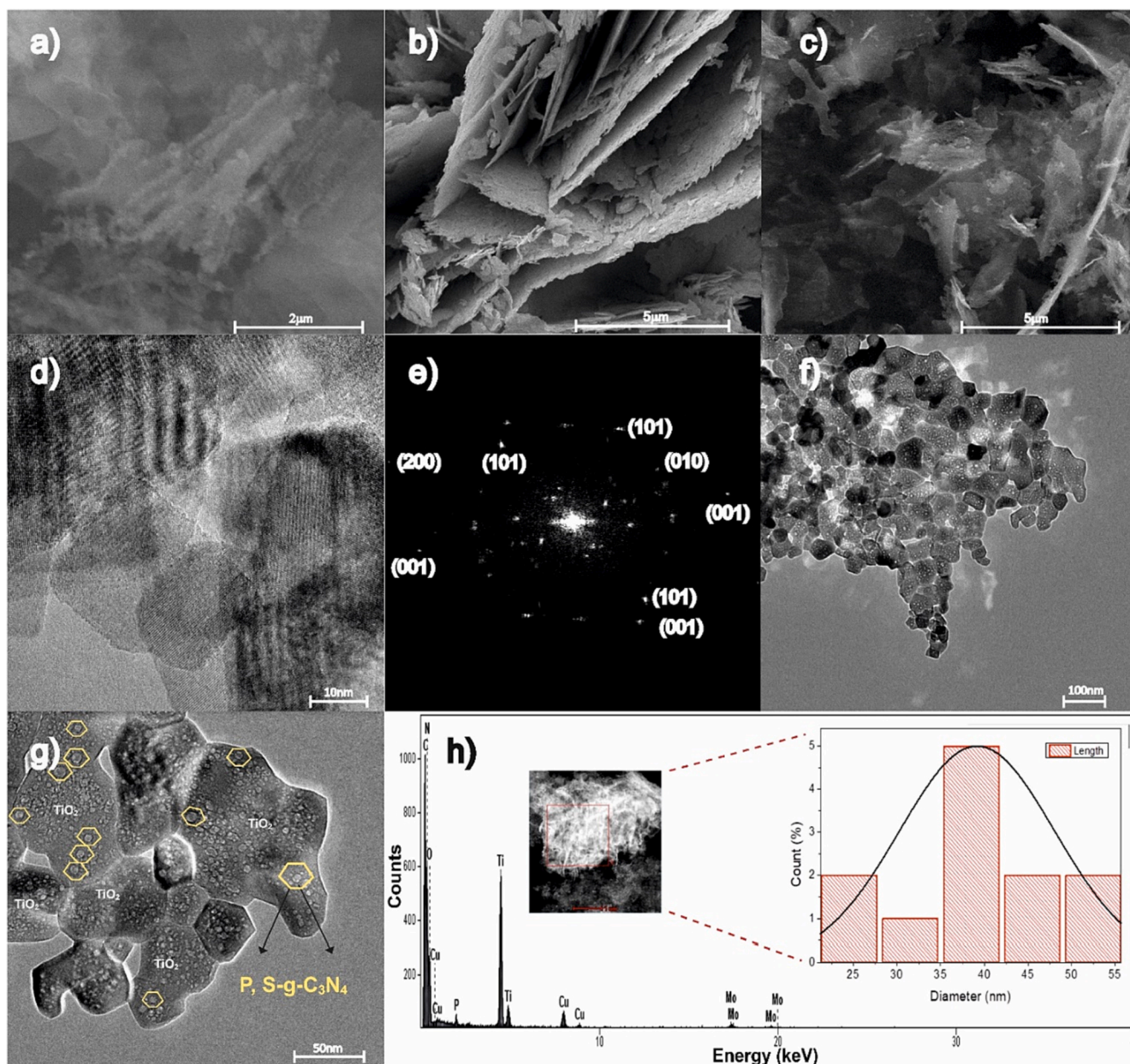


Fig. 3. SEM images of synthesized (P, S)-doped $g\text{-C}_3\text{N}_4$ (a), 2D TiO_2 (b), (P, S)-doped $g\text{-C}_3\text{N}_4/\text{TiO}_2$ (5 %) (c), TEM and corresponding FFT image of 2D TiO_2 nanosheets (d, e), TEM images of (P, S)-doped $g\text{-C}_3\text{N}_4/\text{TiO}_2$ (5 %) (f, g), EDX elemental composition graph and size distribution graph for (P, S)-doped $g\text{-C}_3\text{N}_4/\text{TiO}_2$ (5 %) (h).

TiO_2 (5 %) and (P, S)- $g\text{-C}_3\text{N}_4/\text{TiO}_2$ (10 %).

As presented in Fig. 4, the characteristic peaks for Ti 2p are observed at a binding energy of 464.5 eV (Ti 2p_{1/2}) and 458.5 eV (Ti 2p_{3/2}) and are related to Ti⁴⁺ [49]. The O 1s region could be deconvoluted for three peaks. The major peak at 530.16 eV is related to oxygen in the TiO_2 crystal lattice (Ti—O—Ti). The less intense peaks at 530.96 eV and 531.84 eV are assigned to oxygen in O—H and C=O bonds [36].

The C 1s region could be deconvoluted for three peaks at 284.8, 286.11, and 288.35 (eV) associated with sp² hybridization of C=C bonds, chemical bonding of C—O and sp² hybridization of C in N=C (—N)₂ bond, which directly proved the presence of graphitic carbon nitride in the composition [50]. The observed signals around 398 eV and 400 eV corresponded to the presence of C—N bonding in the carbon nitride network and tertiary nitrogen groups C—(N)₃. Fig. 4e showed that binding energies of 133.8 eV and 134.72 eV corresponding to the peaks of P 2p_{3/2} and P 2p_{1/2} are attributed to the P—N bond, indicating

the substitution of phosphorus in the carbon position and its covalently bonding with the nitrogen of the $g\text{-C}_3\text{N}_4$ framework [51]. The XPS spectra of S 2p showed the presence of two small and broad peaks at 168.64 eV and 169.84 eV (Fig. 4f). Generally, the presence of sulfur can be detected as S 2p at binding energies of 165 and 166 eV [52]. If the obtained value of binding energy is lower than 165 eV, it suggests for S-doped in the position of nitrogen with a rise in the S—C bond, whereas a higher value indicates for S-doped in the position of carbon, giving thus rise in the S—N bond [52,53]. The (P, S)- $g\text{-C}_3\text{N}_4/\text{TiO}_2$ heterocomposite formation results from surface modification than doping and substitution of O atoms with (P, S)-atoms in the TiO_2 lattice since Ti—C bonds (459.4 eV), P—Ti bonds (128.6 eV) and Ti—S bonds (163.4 eV) are not observed based on XPS analysis [54–56]. Meanwhile, the XPS analysis for the most active (P, S)- $g\text{-C}_3\text{N}_4/\text{TiO}_2$ (5 %) photocatalyst confirmed the presence of 25.25 at. % of Ti, 63.60 at. % of O, 7.66 at. % of C, 2.24 at. % of N, 1.05 at. % of P, and 0.21 at. % of S.

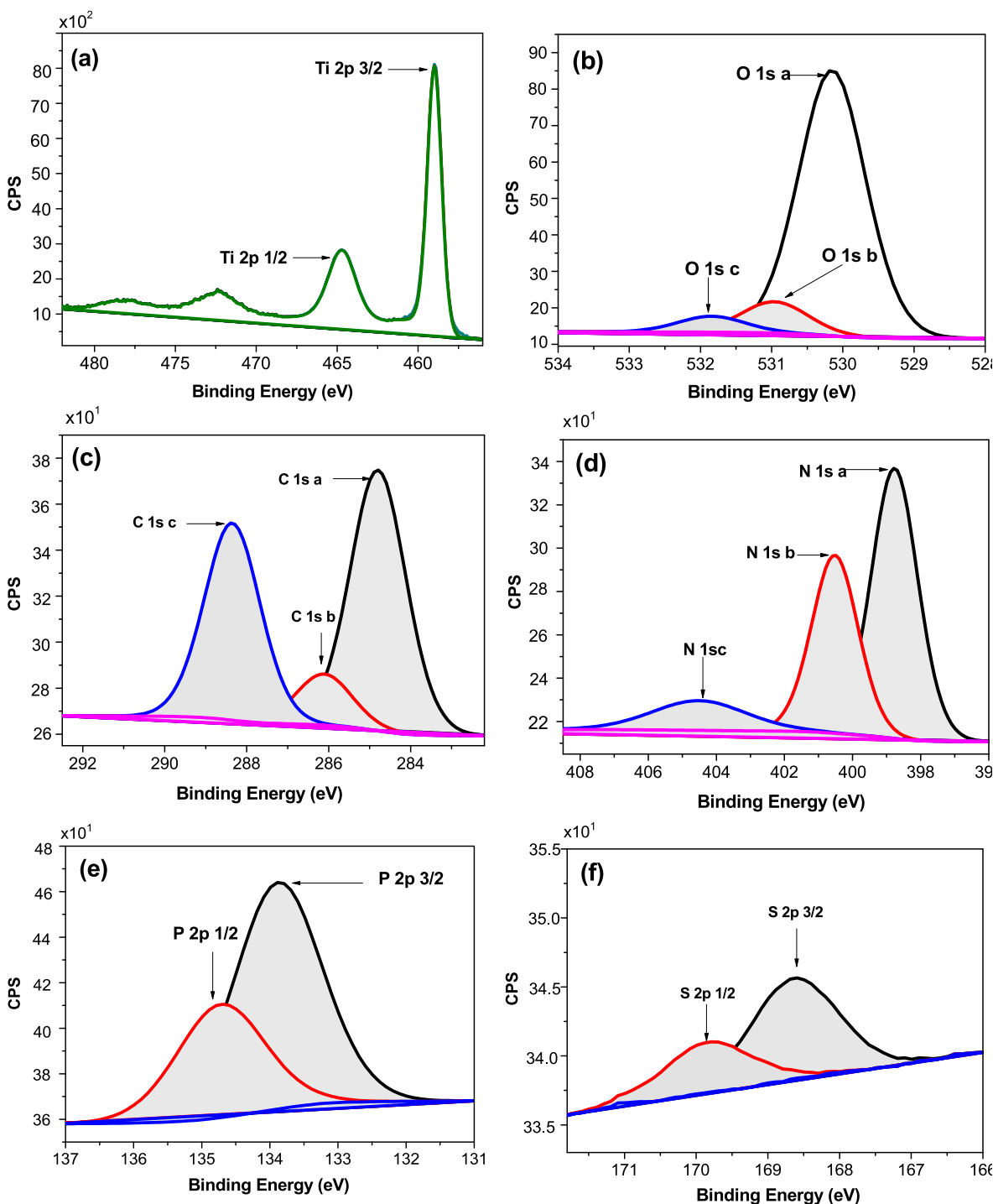


Fig. 4. XPS spectra for Ti 2p (a), O 1s (b), C 1s (c), N 1s (d), P 2p (e), and S 2p (f) signals with Gaussian fits, respectively.

Additionally, X-ray fluorescence spectroscopy (XRF) confirmed the presence of 0.05 % of sulfur in the (P, S)-g-C₃N₄ composite. The XPS spectra for lower (2.5 wt%) and higher amounts (10 wt%) of (P, S)-g-C₃N₄ in the composite of (P, S)-g-C₃N₄/TiO₂ are shown in [Figures S2 and S3](#) in the [Supporting Material](#).

The Raman spectra of 2D TiO₂, (P, S)-doped g-C₃N₄, and (P, S)-doped g-C₃N₄/TiO₂ (5 %) photocatalysts are presented in [Fig. 5](#). The space group of the tetragonal anatase is I4₁/amd, and the local symmetry is D_{2d} which, after group factor analysis, led to the conclusion that in the Raman spectrum, six basic Raman-active modes (A_{1g} + 2B_{1g} + 3E_g) should be observed. The Raman spectrum of TiO₂ showed five bands at

141 (E_g), 195 (E_g), 395 (B_{1g}), 515 (A_{1g}), and 639 (E_g) cm⁻¹. The sixth band, usually observed at about 513 cm⁻¹ (A_{1g}), may not be noticed due to the broadening of the band observed at 515 cm⁻¹. The Raman spectrum of (P, S)-g-C₃N₄ consisted of several peaks of g-C₃N₄ at 478, 708, 752, 982, 1236, and 1315 cm⁻¹, where two of them were most distinguished at 708 and 1236 cm⁻¹, respectively. The peak observed at 708 cm⁻¹ can be assigned as the layer-layer deformation vibrations and at 1236 cm⁻¹ to the =C (sp²) bending vibration [57]. In the hybrid (P, S)-g-C₃N₄/TiO₂ material, only 2 at% of g-C₃N₄ was noticed; therefore, the signal is quite weak, but it is still possible to observe a single, small peak at around 708 cm⁻¹ on the slope of the TiO₂ E_g band (639 cm⁻¹).

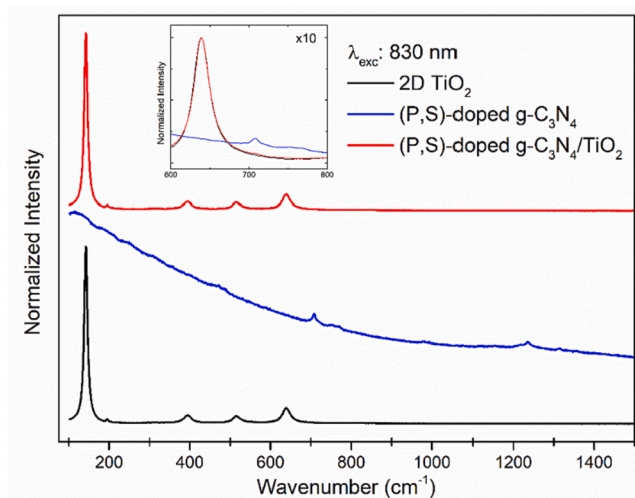


Fig. 5. Raman spectra of the 2D TiO₂, (P, S)-doped g-C₃N₄, and (P, S)-doped g-C₃N₄/TiO₂ (5 %) powders recorded with the 830 nm excitation wavelength.

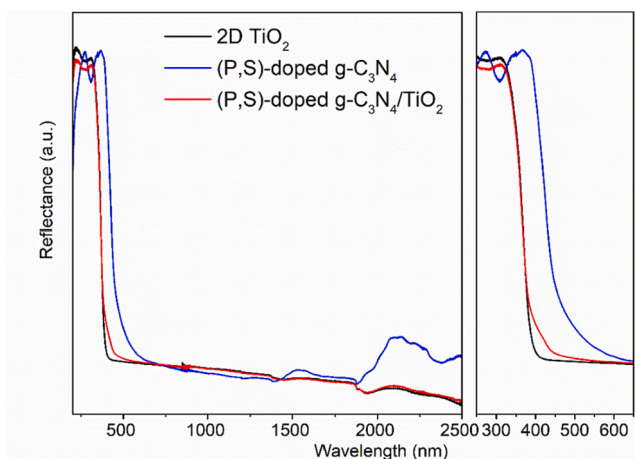


Fig. 6. Reflectance spectra of the TiO₂, (P, S)-doped g-C₃N₄ and (P, S)-doped g-C₃N₄/TiO₂ (5 %) photocatalysts.

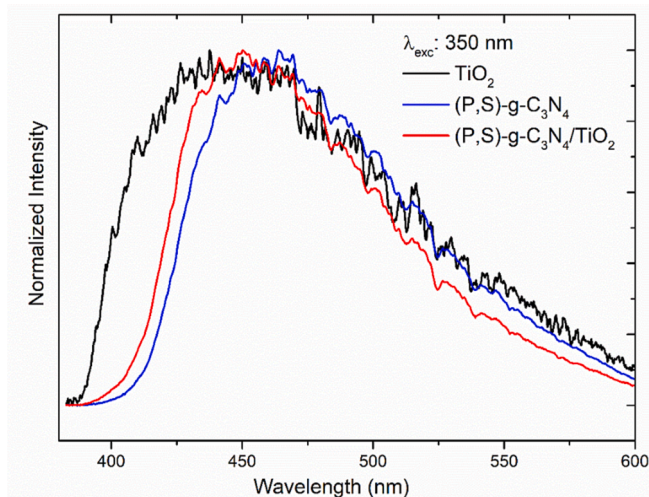


Fig. 7. Luminescence spectra of the 2D TiO₂, (P, S)-doped g-C₃N₄, and (P, S)-g-C₃N₄/TiO₂ (5 %) photocatalysts under UV excitation.

The optical properties of photocatalysts were studied using UV–vis diffuse reflectance spectroscopy and are presented in Fig. 6. The TiO₂ nanosheets display a typical absorption edge at about 395 nm, corresponding to the bandgap of 3.15 eV [58]. The reflectance spectra of (P, S)-g-C₃N₄ consist of a band similar to a typical semiconductor absorption spectrum between 200 and 450 nm, originating from the charge transfer from a populated valence band of a nitrogen atom (2p orbitals) to a conduction band of carbon atom (2p orbitals) of carbon nitride. For the (P, S)-doped g-C₃N₄ structure, the absorption edge is observed at about 510 nm, corresponding to the bandgap of 2.42 eV, which is redshifted compared to the pure g-C₃N₄, where the absorption edge is observed at 480 nm (2.60 eV). The stronger visible-light absorption of (P, S)-g-C₃N₄ showed the possibility of more efficient utilization of sunlight for photocatalysis. In the case of the (P, S)-g-C₃N₄/TiO₂ hybrid material, it can be observed that the absorption band of TiO₂ is broadened, and the sideband corresponds to the absorption of (P, S)-g-C₃N₄.

The emission spectra of all structures showed a broad band in the spectral range from 400 to 600 nm, see in Fig. 7. It can be observed that the 2D TiO₂ emission band is broader than the (P, S)-doped g-C₃N₄ and the hybrid structure of (P, S)-doped g-C₃N₄/TiO₂. For the TiO₂ emission spectrum, the high-energy region of the band corresponds to the indirect band-to-band recombination across the bandgap, and the luminescence in the low-energy range is attributed to excitons that result from surface oxygen vacancies and defects. The (P, S)-doped g-C₃N₄ luminescence spectrum showed the typical band of an organic semiconductor with a strong emission peak at about 470 nm, which is caused by the transition between lone pair to π^* conduction band. The hybrid structure emission spectrum showed the combination of the 2D TiO₂ and (P, S)-g-C₃N₄ luminescence properties. The band is narrower, as for (P, S)-g-C₃N₄, and blueshifted, as for TiO₂. It resulted from reducing the electron density of the π state conjugated system or lone pair state of g-C₃N₄ by the TiO₂ particles that were also previously observed for the boron-doped g-C₃N₄ [59].

The decay times of 2D TiO₂, (P, S)-doped g-C₃N₄ and the hybrid structure were measured using a 50 ns time window (see Fig. 8). In all the cases, non-exponential decay was observed. In the TiO₂ powder, the interaction between electrons and holes was weak because of its indirect-gap band structure; therefore, in the decay profile, a rapid decrease in hole population followed by long-lived electron decay is observed [60]. The luminescence decay of (P, S)-g-C₃N₄ was fitted using three components. The short-living components are associated with the recombination of the electron-hole pairs, and the longer decay can be assigned to the fast separation of electron-hole pairs [61]. Interestingly, although in the (P, S)-doped g-C₃N₄/TiO₂ is only 5 % of (P, S)-g-C₃N₄, the luminescence decay is more similar to the nitride than to oxide. It can also be observed that the decay times are slightly shorter for the hybrid material than for pure (P, S)-g-C₃N₄ (Table 2). Another fact worth noticing is that under 405 nm excitation (absorption maximum of (P, S)-g-C₃N₄ and sideband of (P, S)-g-C₃N₄/TiO₂, the decays are prolonged, and in the case of hybrid photocatalyst can be again observed the long decay component associated with electrons decay (Table 2). From the obtained results, it can be observed that heterojunction formation resulted in better separation of electron-hole pairs.

Fig. 9a shows the Nyquist impedance plot for (P, S)-g-C₃N₄, 2D TiO₂ and (P, S)-g-C₃N₄/2D TiO₂ (5 %). From Nyquist plots, a small semi-circular diameter indicates lower $e^- - h^+$ recombination and high electrical conductivity. The results suggested that the combination of (P, S)-g-C₃N₄ and 2D TiO₂ reduced the charge transfer resistance and enhanced the separation efficiency of photogenerated charge carriers.

Furthermore, to study the surface properties of (P, S)-g-C₃N₄, 2D TiO₂ and (P, S)-g-C₃N₄/TiO₂ (5 %) photocatalysts, the electrophoretic mobility in a function of pH (zeta potential) was investigated (see Fig. 9b).

For $\text{pH} < \text{pH}_{\text{IEP}}$ the surface of photocatalysts was positively charged, while for $\text{pH} > \text{pH}_{\text{pzc}}$ the surface of the photocatalyst was negatively charged. Regarding the preparation procedure, the pH ranging from 4 to

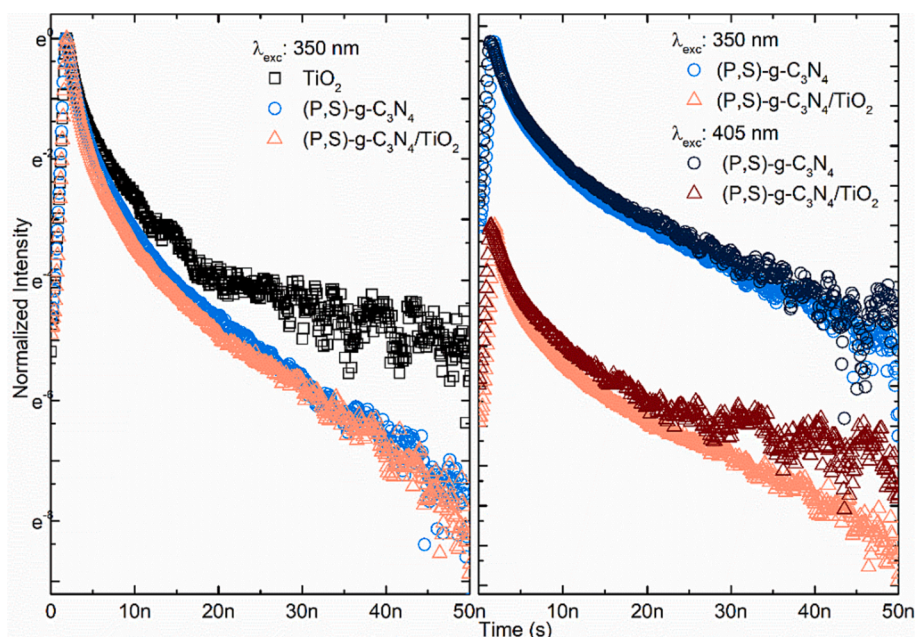


Fig. 8. Luminescence decay curves registered for the TiO_2 , (P, S)- $\text{g-C}_3\text{N}_4$, and (P, S)-doped $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) photocatalysts under two different excitation wavelengths.

Table 2

Decay times were calculated for 2D TiO_2 , (P, S)- $\text{g-C}_3\text{N}_4$, and (P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) photocatalysts under two different excitation wavelengths.

Decay times (ns)			
	TiO_2	(P, S)- $\text{g-C}_3\text{N}_4$	(P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$
$\lambda_{\text{exc}}: 350 \text{ nm}$			
τ_1	0.81	0.68	0.6
τ_2	4.49	2.45	2.13
τ_3	207	8.69	7.31
$\lambda_{\text{exc}}: 405 \text{ nm}$			
τ_1	–	0.92	1.25
τ_2	–	2.99	4.61
τ_3	–	10.9	125

6 is proper for the heterojunction formation since the negatively charged surface of (P, S)- $\text{g-C}_3\text{N}_4$ could come in contact with positively charged 2D TiO_2 via electrostatic attractions to form the composites; hence, phosphorus and sulfur co-doped carbon nitride are layered upon 2D TiO_2 nanosheet. Besides, during the photodegradation process, based on zeta potential measurements, higher stability of suspension can be

noticed at a pH of about 5 and above 7. In the natural environment, pH ranges from 6 to 7. The pKa value of CBZ is 13.9 and ACT is about 9.5. Therefore, CBZ will primarily be present in its protonated form (pH < pKa), while acetaminophen is largely unionized over the neutral range of pH.

Furthermore, the optical properties of the most efficient (P, S)- $\text{g-C}_3\text{N}_4/2\text{D TiO}_2$ (5 % wt) photocatalyst suspension and 2D TiO_2 for comparison were evaluated by means of photon flux measurements. The UVA spectral-average mass extinction coefficient (β) and mass absorption coefficient (κ) were determined for suspensions of both powders, followed by calculation of the scattering coefficient (σ) and albedo (ω) Fig. 10 (a, b) [39]. Based on the obtained values, the local volume rate of photon absorption (LVRPA) was calculated numerically for a cross-section of the reactor, following the six-flux model approach [41] with the scattering probabilities adapted from reported studies of TiO_2 , based on the Henyey-Greenstein phase function (details [62]). Finally, integration of the LVRPA values over the analyzed cross-section was performed to obtain the total rate of the photon absorption (TRPA) for a unit of reactor height and was compared with the incident photon flux value.

Obtained data have shown that modification of 2D TiO_2 with 5 % (P, S)- $\text{g-C}_3\text{N}_4$ has a very limited effect on the optical properties of the

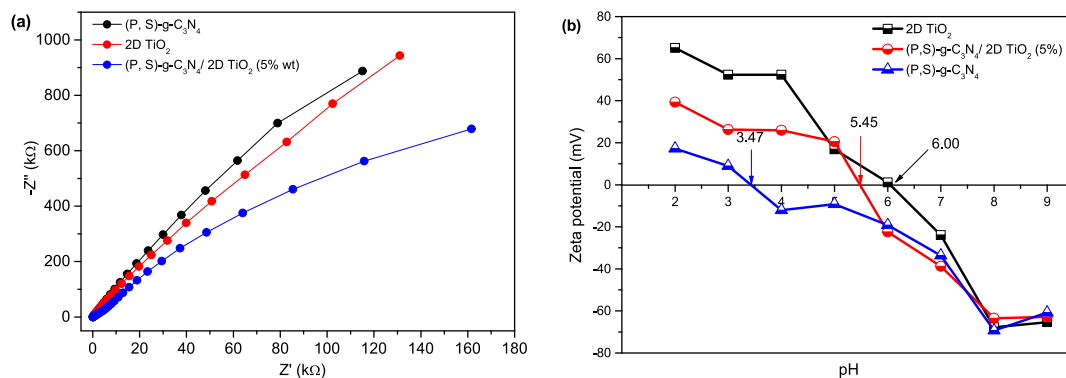


Fig. 9. EIS Nyquist plots for (P, S)- $\text{g-C}_3\text{N}_4$, 2D TiO_2 and (P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) (a), zeta potential determined from the electrophoretic mobility in dependence of the pH, $I = 1 \cdot 10^{-2}$ M KCl (b).

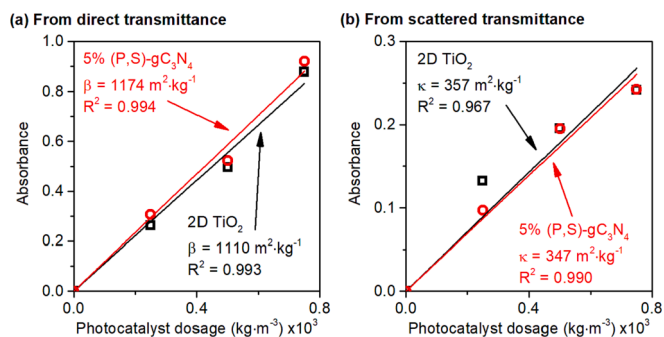


Fig. 10. Dependence of the UVA spectral-average absorbance of the photocatalyst suspension on the photocatalyst dosage, obtained from the transmittance measurements: (a) without including scattered part of the radiation and (b) including radiation scattered through the suspension. Beta and kappa values are slopes of the fitted lines.

suspension. This is followed by almost identical LVRPA distribution inside the reactor, which was plotted for the used concentration (1 g/dm^3) Fig. 11 (a, b). For both materials, the TRPA essentially achieves a quite stable value of 2 W/m^2 for this concentration, with only a slight, linear increase observed with further increase of the photocatalyst dosage Fig. 11 (c). In both cases, approximately 90 % of all UVA photons introduced to the system should be absorbed at 1 g/dm^3 .

Following obtained results, it can be assumed that the observed activity increase does not result from the better UVA light absorption of the composite. Furthermore, since (P, S)-g-C₃N₄ compose only 5 % of the final material, the electronic interactions between both components should be mostly responsible for the observed activity enhancement, which was also evidenced by other techniques.

3.2. Photocatalytic degradation of carbamazepine (CBZ) and acetaminophen (ACT)

The photocatalytic activity of prepared photocatalysts was studied in the degradation of carbamazepine and acetaminophen, pharmaceuticals belonging to the group of emerging contaminants, which are not susceptible to biological degradation. As shown in Fig. 12a, doping the graphitic carbon nitride by phosphorus and sulfur increased the photocatalytic activity in the reaction of carbamazepine degradation. The degradation increased from 49 % for g-C₃N₄ to almost 100 % for (P, S)-g-C₃N₄ within 120 min of irradiation, while the TOC values presented in Table S1 (Supporting Material) were 14 % and 18 %, respectively. Moreover, the combination of (P, S)-g-C₃N₄ and 2D TiO₂ significantly improved the removal of carbamazepine from the aqueous phase. Furthermore, the observed degradation efficiency of g-C₃N₄/TiO₂ (5 %) was markedly lower compared to all obtained (P, S)-doped g-C₃N₄/TiO₂ composites, confirming the positive effect of (P,S) co-doping of g-C₃N₄, as presented in Figure S6 in the Supporting Material. For example, the time needed to complete degradation of carbamazepine was 2-times lower for g-C₃N₄/TiO₂ (5 %) than (P, S)-g-C₃N₄/TiO₂ (5 %), and the mineralization efficiency was 42 % and 76 %, respectively. Among the series of (P, S)-g-C₃N₄/TiO₂ photocatalysts, (P, S)-doped g-C₃N₄/TiO₂ (5 %) composite revealed the highest photodegradation efficiency of about 95 % within only 15 min of irradiation. After 30 min of irradiation, complete carbamazepine photodegradation was noticed. The kinetics of reaction for CBZ degradation in the presence of the photocatalysts was studied, and the reactions fit the model of first-order kinetics ($R^2 > 0.97$) (see Fig. 12b).

From kinetics modeling results, it was proved that doping of carbon nitride with phosphorus and sulfur increased the photocatalytic efficiency, and preparation of composites of (P, S)-g-C₃N₄/TiO₂ increased the synergy of reaction, which resulted in complete and fast degradation

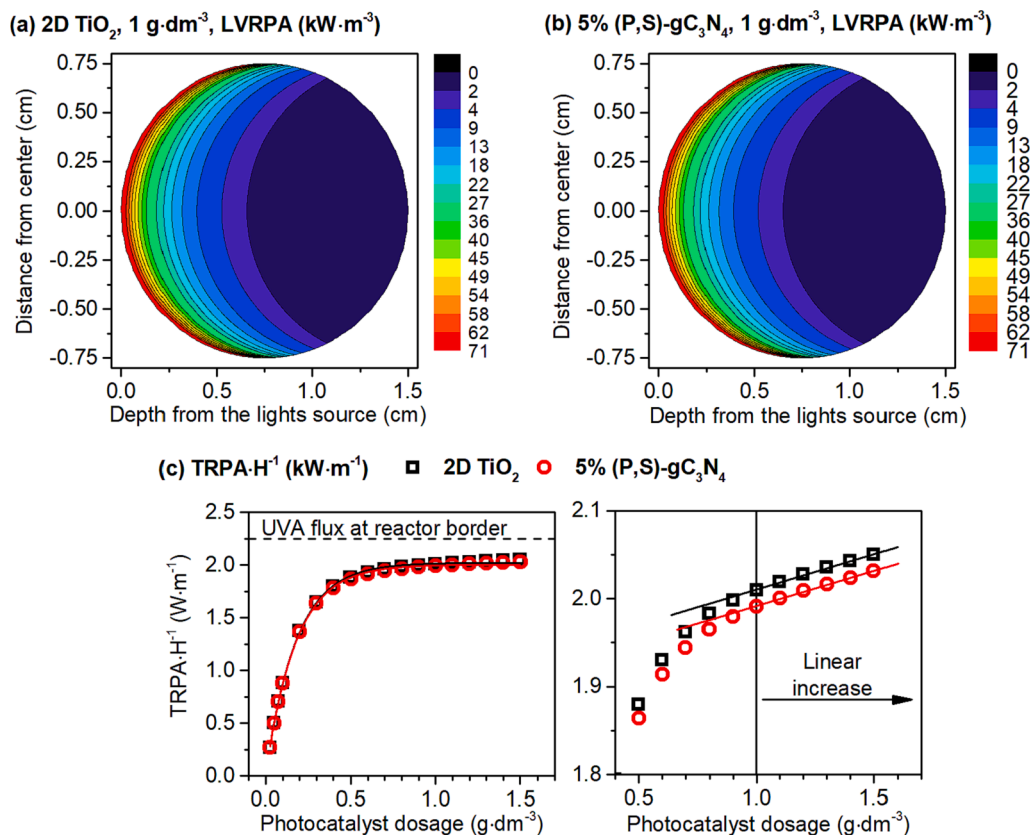


Fig. 11. LVRPA distribution in the cross-section of photoreactor for the control 2D TiO₂ (a) and (P, S)-g-C₃N₄/ 2D TiO₂ (5 % wt) (b); integrated LVRPA values for the analyzed cross section as the function of possible photocatalyst-dosage (c).

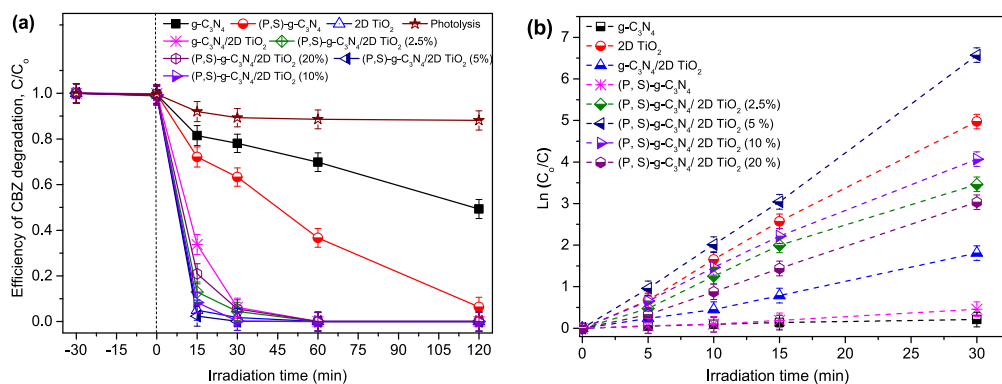


Fig. 12. The efficiency of carbamazepine photodegradation (a), photodegradation kinetics curves for the most active photocatalysts (b). Experimental conditions: $C_{CBZ} = 14 \text{ mg}\cdot\text{dm}^{-3}$, photocatalyst loading of $1 \text{ g}\cdot\text{dm}^{-3}$, water temperature $20 \text{ }^\circ\text{C}$, neutral pH, and 120 min of UV–vis light irradiation.

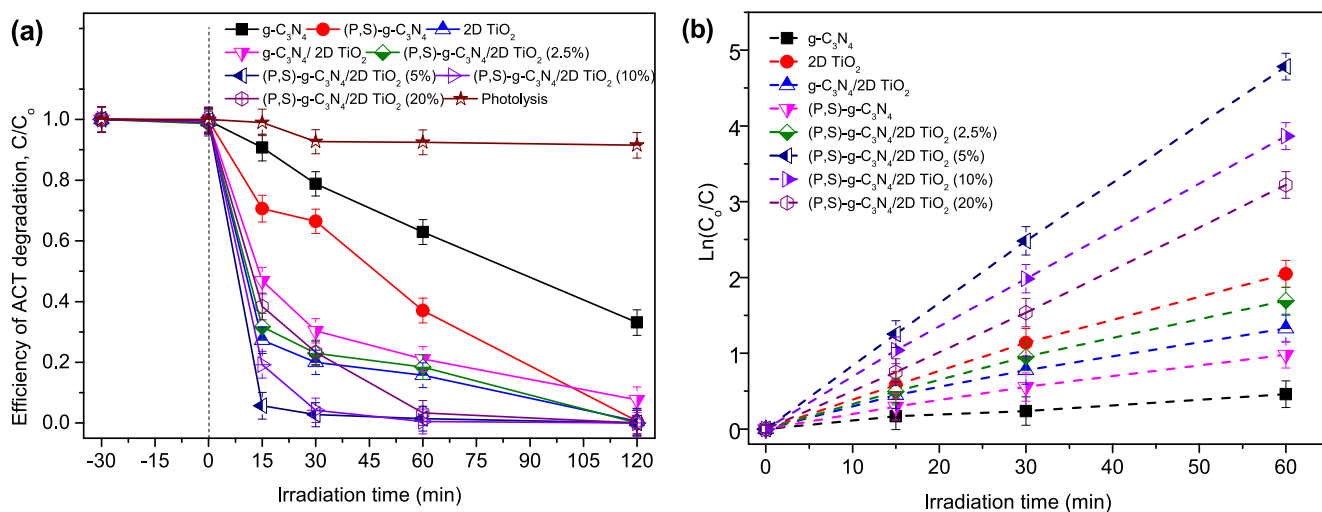


Fig. 13. The efficiency of acetaminophen photodegradation (a), photodegradation kinetics curves for the most active photocatalysts (b). Experimental conditions: $C_{ACT} = 20 \text{ mg}\cdot\text{dm}^{-3}$, photocatalyst loading of $1 \text{ g}\cdot\text{dm}^{-3}$, water temperature $20 \text{ }^\circ\text{C}$, neutral pH, and 120 min of UV–vis light irradiation.

of CBZ. Specifically, the lowest rate constant was observed for undoped $g-C_3N_4$ (see Table S1). The phosphorus and sulfur co-doping of $g-C_3N_4$ increased the rate constant to 4-fold. For the most active photocatalyst of (P, S)- $g-C_3N_4/TiO_2$ (5 %), the degradation rate constant was 0.203 min^{-1} , compared to lower degradation of (P, S)- $g-C_3N_4/TiO_2$ (10 %), (P, S)- $g-C_3N_4/TiO_2$ (2.5 %), and $2D TiO_2$ with a rate constant of 0.161 min^{-1} , 0.133 min^{-1} , and 0.128 min^{-1} , respectively.

Furthermore, it was noticed that acetaminophen is more persistent than carbamazepine, hence degradation time needed to remove this pharmaceutical from the solution completely was 2-times longer (see Fig. 13). The pure $2D TiO_2$ possessed a higher rate constant of 0.029 min^{-1} than (P, S)- $g-C_3N_4$, and the combination of both photocatalysts resulted in increased rate constants and activity (see Table S2 in the Supporting Material). Besides, the acetaminophen degradation tests confirmed the best photocatalytic activity of (P, S)- $g-C_3N_4/TiO_2$ (5 %) with 99.5 % degradation efficiency, the highest rate constant of 0.074 min^{-1} , and TOC removal of 40 % after 60 min of irradiation.

Among composite materials, the lowest photoactivity was observed for (P, S)- $g-C_3N_4/TiO_2$ (2.5 %), with 85 % degradation after 60 min of irradiation, rate constant of 0.031 min^{-1} , and TOC removal of 35 % with a synergy index of 0.68 (see in Table S2). The photocatalytic activity was followed by (P, S)- $g-C_3N_4/TiO_2$ (10 %) and (P, S)- $g-C_3N_4/TiO_2$ (20 %) with 98.5 % and 97 % of ACT removal, and corresponding synergy indexes of 1.62 for (P, S)- $g-C_3N_4/TiO_2$ (5 %), 1.41 for (P, S)- $g-C_3N_4/TiO_2$ (10 %) and 1.18 for (P, S)- $g-C_3N_4/TiO_2$ (20 %). Below and above the optimum amount of (P, S)- $g-C_3N_4$ (5 %) combined with $2D TiO_2$, the

degradation rate constants decreased to 0.064 min^{-1} , 0.054 min^{-1} and 0.031 min^{-1} for (P, S)- $g-C_3N_4/TiO_2$ (10 %), (P, S)- $g-C_3N_4/TiO_2$ (20 %), and (P, S)- $g-C_3N_4/TiO_2$ (2.5 %) composites, respectively. Similarly, the effect of phosphorus and sulfur co-doping into $g-C_3N_4$ proved to be effective in ACT removal, see Figure S6 in the Supporting Material. The higher degradation efficiency was observed for (P, S)- $g-C_3N_4$ (63 %) compared to undoped $g-C_3N_4$ (12 %) after 60 min of irradiation. Furthermore, the photocatalytic activity of (P, S)- $g-C_3N_4/TiO_2$ (5 %) was compared with TiO_2 P25 as a standard photocatalytic material. The improved photocatalytic activity under UV–vis light was observed for (P, S)- $g-C_3N_4/TiO_2$ (5 %) composite, as shown in Figure S7 in the Supporting Material.

3.3. Influence of key factors – The effect of water matrix, initial pH, pollutant concentration and photocatalyst dosage

Firstly, the role of different inorganic anions and the pH of the aqueous phase were investigated. Sodium sulfite (Na_2SO_3), sodium sulfate (Na_2SO_4), sodium nitrate ($NaNO_3$), sodium chloride ($NaCl$), and sodium carbonate (Na_2CO_3) in a concentration of 0.1 mM were used as the source of inorganic anions present in the aqueous systems. The photocatalytic degradation efficiency in the absence of anions was 95 % within 15 min and 100 % within 30 min under UV–vis light irradiation. In the presence of monovalent anions of Cl^- and NO_3^- , the irradiation time needed to achieve above 99 % degradation increased 2-times, as presented in Table S3. The presence of Cl^- and NO_3^- inhibited the CBZ

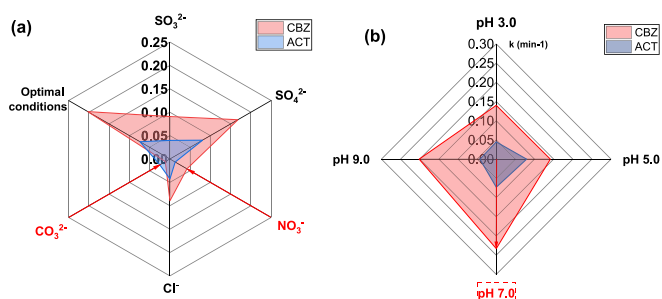


Fig. 14. Radial graphs of water matrix effect (a), pH effect (b) for photo-degradation of CBZ and ACT.

degradation process due to the high adsorption affinity of monovalent anions for the composite surface. The rate constants decreased from 0.203 min^{-1} to 0.089 and 0.042 min^{-1} , respectively. Since the photocatalytic process belongs to the radical pathway, this means that the monovalent anions will compete to occupy the active sites in the composite, scavenging thus the hydroxyl and superoxide radicals, which are the main radical species responsible for the degradation of CBZ. Regarding the presence of divalent anions of SO_4^{2-} and CO_3^{2-} , the irradiation time to completely degrade CBZ increased from 30 min to 60 min, whereas the rate constant decreased to 0.168 min^{-1} and 0.112 min^{-1} , see Fig. 14a. Therefore, it can be concluded that the presence of divalent anions in the water phase has a moderate effect on the inhibition of CBZ degradation.

Furthermore, the effect of pH on CBZ degradation in the presence of (P, S)-doped $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) composite was studied. The degradation efficiency of CBZ at pH 3, 5, 7, and 9 was found to be 98.5 %, 98.5 %, 100 %, and 100 % within 30 min of irradiation. The corresponding rate constants equaled 0.140 min^{-1} , 0.141 min^{-1} , 0.203 min^{-1} , and 0.201 min^{-1} . Apparently, as presented in Fig. 14b, the neutral and alkaline conditions are more favorable for the degradation of CBZ in the presence of (P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ photocatalyst due to higher stability of photocatalyst suspension and attraction between the negatively charged photocatalyst surface ($\text{pH} > \text{pH}_{\text{IEP}}$) and protonated form of carbamazepine.

Regarding ACT degradation, the presence of NO_3^- and CO_3^{2-} inhibited the efficiency of the photocatalytic reaction. The efficiency of ACT degradation equaled 69 % and 68.5 % in 60 min of irradiation compared to 99.5 % degradation in the absence of inorganic anions.

The presence of SO_4^{2-} slightly improved the degradation of ACT with 100 % and a rate constant of 0.080 min^{-1} , whereas the presence of Cl^- slightly decreased the degradation to 91 % with a rate constant of 0.042 min^{-1} . The effect of inorganic anions was compared for 60 min since

total degradation was achieved in 120 min for all the samples. Detailed results on the effect of inorganic anions and pH are presented in Table S3. It was observed that the optimal conditions for ACT photo-degradation are a pH range between 5 and 7, with a degradation efficiency of almost 100 % in 60 min of irradiation. The rate constants values were 0.079 for pH of 5 and 0.074 min^{-1} for pH of 7.

Furthermore, the effect of ACT and CBZ concentration on the efficiency of the photodegradation process in the presence of (P, S)-doped $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) composite was also studied. Primary concentrations of CBZ and ACT were doubled to $28 \text{ mg}\cdot\text{dm}^{-3}$ and $40 \text{ mg}\cdot\text{dm}^{-3}$, respectively. It was found that the increase of CBZ concentration from $14 \text{ mg}\cdot\text{dm}^{-3}$ to $28 \text{ mg}\cdot\text{dm}^{-3}$ resulted in the decrease of CBZ degradation efficiency from 100 % to 84 % in 30 min of the degradation process, while the degradation rate decreased from 0.20 min^{-1} to 0.15 min^{-1} . Similarly, for ACT degradation, increasing the pharmaceutical concentration resulted in a decrease of ACT degradation efficiency from 100 % to almost 70 % within 120 min of irradiation, while the degradation rate decreased from 0.07 min^{-1} to 0.03 min^{-1} . However, significant differences are observed comparing the efficiency of TOC removal for the double concentration of the pharmaceuticals in water. The TOC removal efficiency measured as TOC/TOC_0 decreased from 72 % to 7 % for CBZ degradation and from 40 % to 3 % for ACT degradation process, as presented in Table S4 in the Supporting Material. The markedly lower TOC removal efficiency is associated with the formation of by-products.

The effect of photocatalyst amount of 0.5, 1.0, and $2.0 \text{ g}\cdot\text{dm}^{-3}$ was studied for the removal of CBZ and ACT in their primary concentrations of $14 \text{ mg}\cdot\text{dm}^{-3}$ and $20 \text{ mg}\cdot\text{dm}^{-3}$, respectively. No significant differences were noticed regarding the efficiency of pharmaceuticals degradation. Nevertheless, a slightly higher degradation rate was observed for a photocatalyst amount of

$1.0 \text{ g}\cdot\text{dm}^{-3}$, defining it as the optimal photocatalyst dosage, as presented in Table S5 in the Supporting Material. The result regarding the effect of photocatalyst amount was found to be coherent with photon flux measurements.

3.4. Degradation pathway of carbamazepine (CBZ) and acetaminophen (ACT) and mechanism of photodegradation

Since the best photocatalytic activity was revealed for the composite of (P, S)-doped $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %), the identification of reactive oxygen species responsible for the degradation of CBZ and ACT was performed for the referred composite, as shown in Fig. 15. The results demonstrated that the photocatalytic degradation of CBZ and ACT in the presence of (P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) was highly inhibited in the presence of *para*-benzoquinone (P-BQ) and isopropanol, which are used as superoxide radicals (O_2^-) and hydroxyl radicals (HO^\cdot) scavengers. For carbamazepine degradation, in the presence of P-BQ, the efficiency of the reaction

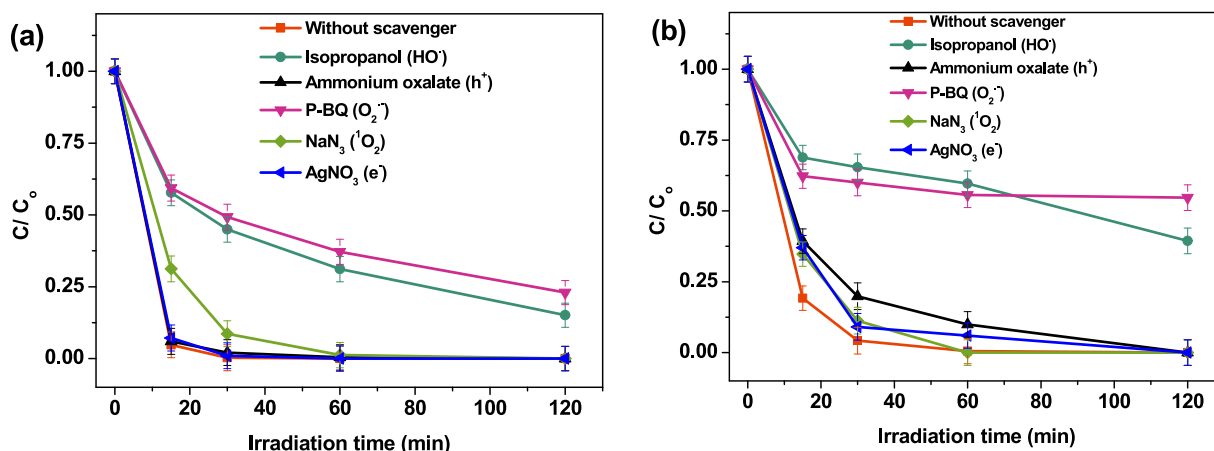


Fig. 15. The degradation efficiency of (P, S)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (5 %) in the presence of scavengers for carbamazepine (a) and acetaminophen (b).

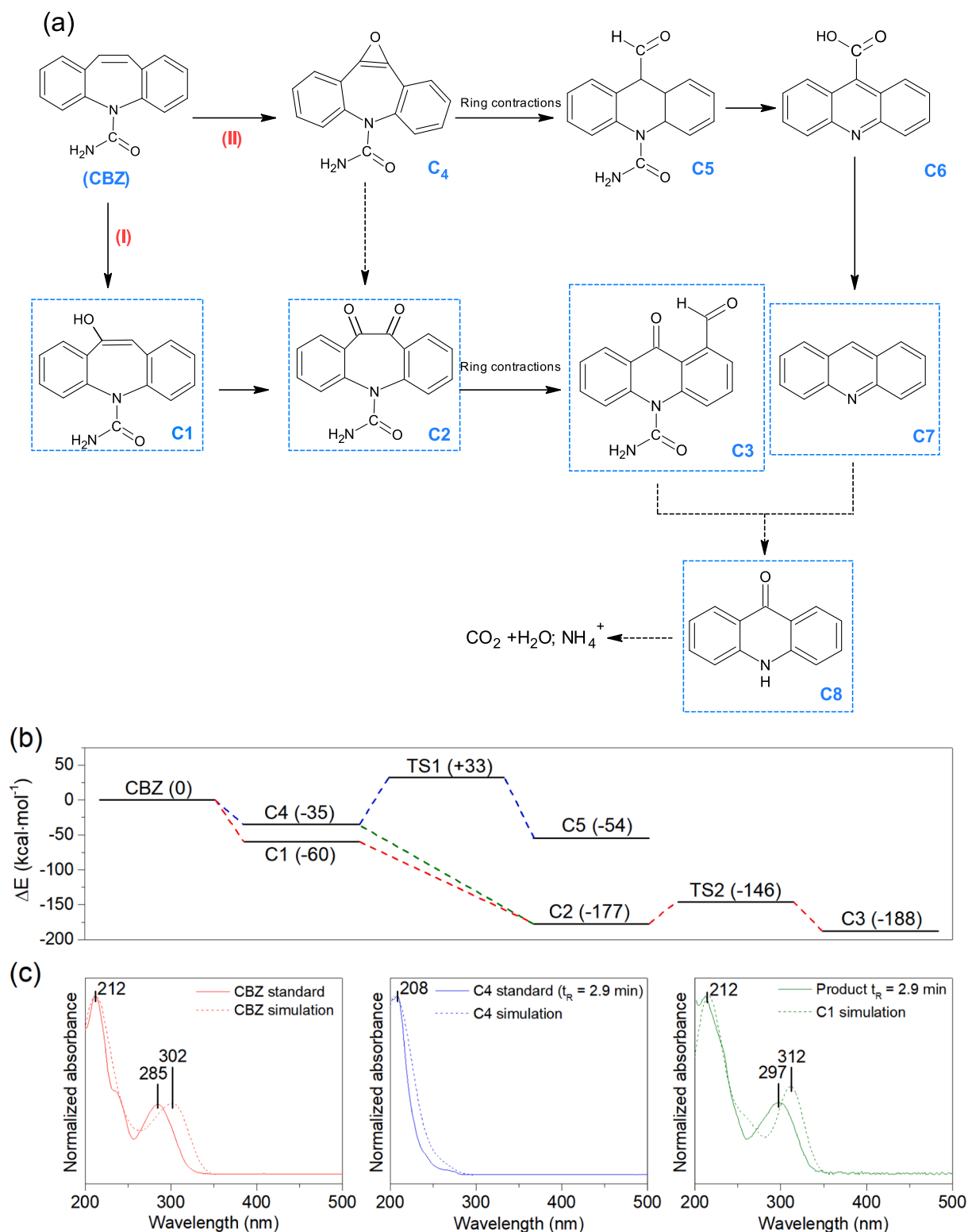


Fig. 16. The proposed mechanism of carbamazepine (a) photocatalytic degradation, together with calculated energy path of the suggested routes (b) and comparison between simulated and observed absorption spectra of the selected compounds (c). Little, consistent shifts of the lower-energy maxima compared in panel (c) result most likely from a bit different environment applied during the HPLC-DAD analysis, which was not simulated in detail.

decreased from 100 % in 30 min to 77 % in 120 min, and the rate constant decreased by 16-fold for the reaction proceeded in the presence of P-BQ and 13-fold in the presence of isopropanol as a $\cdot\text{OH}$ scavenger. Also, the degradation of ACT decreased from 100 % to 45 % in the presence of P-BQ as an O_2^- scavenger. The introduction of isopropanol

inhibited the removal efficiency of ACT to 60.5 % within 120 min of irradiation. The rate constant was 15 times lower than the rate constant for the reaction system in the absence of O_2^- scavenger; meanwhile, the rate constant decreased 10 times in the presence of $\cdot\text{OH}$ scavenger.

The responsible reactive oxidation species for the degradation of CBZ

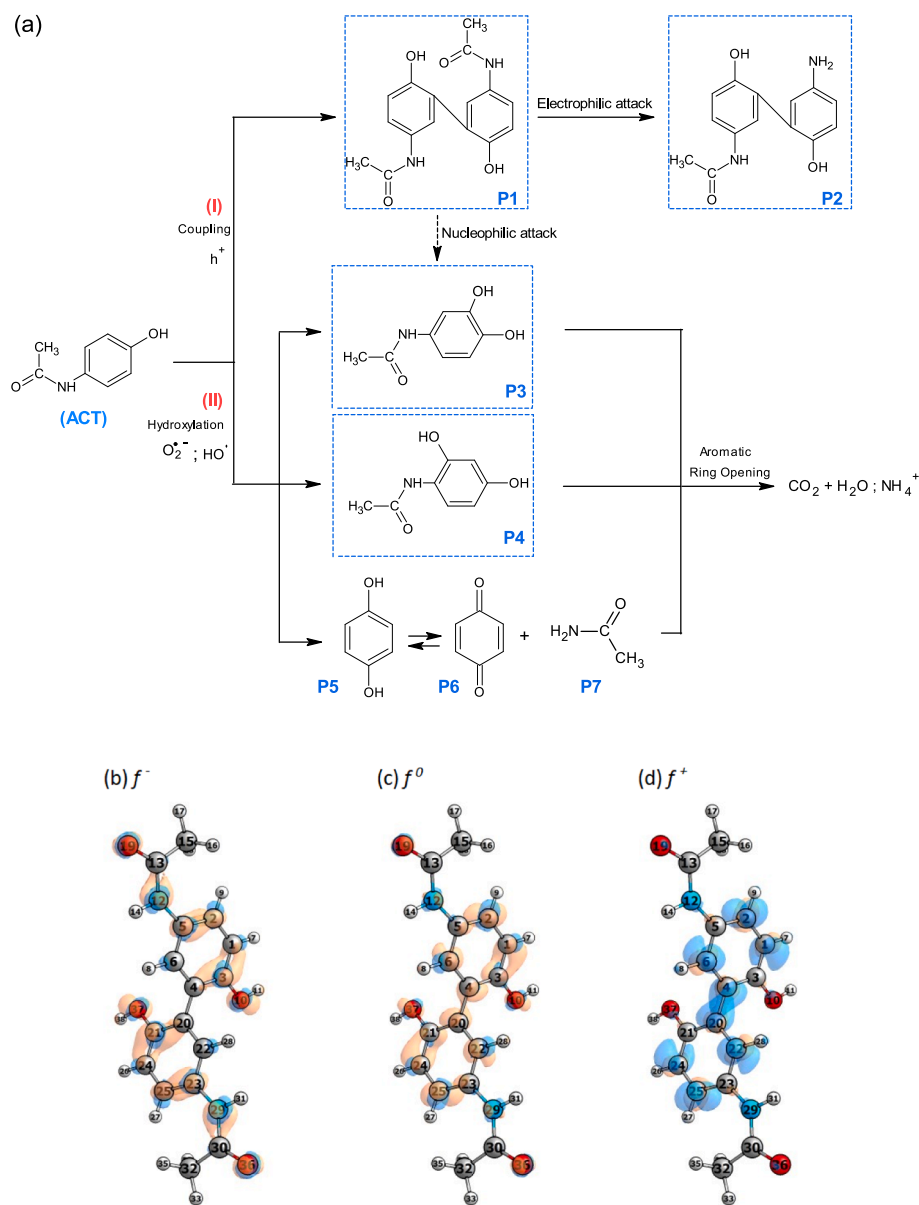


Fig. 17. The proposed mechanism of acetaminophen photocatalytic degradation (a) and calculated maps of Fukui function for compound [P1] (b-d). Carbons, hydrogens, oxygens and nitrogens are grey, white, red and blue spheres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and ACT were superoxide radicals ($O_2^{\cdot-}$) and hydroxyl radicals (HO^{\cdot}). Identification of carbamazepine (CBZ) intermediates was performed using LC-MS analysis in combination with additional DFT calculations of the possible by-products formation. Based on the obtained results, the route (I) of CBZ removal was proposed, as presented in Fig. 16a, which especially includes the formation of hydroxy-carbamazepine [C1; m/z 271.1] as the initial product. Further degradation of [C1] leads to the formation of dioxo carbamazepine [C2, m/z 266.7], which was clearly observed in the MS spectra. These results are in agreement with the performed DFT calculations, which have shown that [C2] is a very stable compound compared to the initial CBZ molecule balanced with the H_2O and O_2 as possible substrates/by-products. Interestingly, this route seems much more probable than alternative path (II), which includes the formation of carbamazepine-10,11-epoxide [C4; m/z 271.1], both due to the possible energy effect (shown in Fig. 16b), as well as lack of the [C4] signals observed on the DAD spectra (Fig. 16c).

In this regard, path (I) is proposed as the main route of CBZ degradation in the presence of (P, S)-g-C₃N₄/TiO₂ (5 %) composite.

Furthermore, both [C2] and [C4] are also stabilized by the possible ring contraction, forming acridine derivatives as possible by-products. In this case, rearrangement of [C4] to [C5] also seems less probable, as the energy barrier is visibly higher than for the [C2]-[C3]. However, it is noteworthy that this energy barrier [C4]-[C5] can be still overcome by photon absorption ($E_{\text{barrier}} = 2.95$ eV), which would fit previous reports showing acridine [C7; m/z 179.6] as an important product of CBZ photolysis [63], also observed in this study. Both acridine [C7] and rearranged [C3] might easily form acridone [C8; m/z 195.6], which was the final observed by-product. Further oxidation and ring-opening of [C8] may generate short-chain carboxylic acids, and lastly CO_2 , H_2O and NH_4^+ may be formed as mineralization products [64].

The degradation pathway of ACT and identified by-products are presented in Fig. 17a. Degradation pathway of ACT follows two main routes, the coupling (I) and hydroxylation/oxidation route (II), with main observed products [P1; m/z 300.7], [P3; m/z 167.5] and [P4; m/z 167.5]. The route (II) ascribed to hydroxylation/oxidation shows transformations typical for the photocatalytic degradation of different

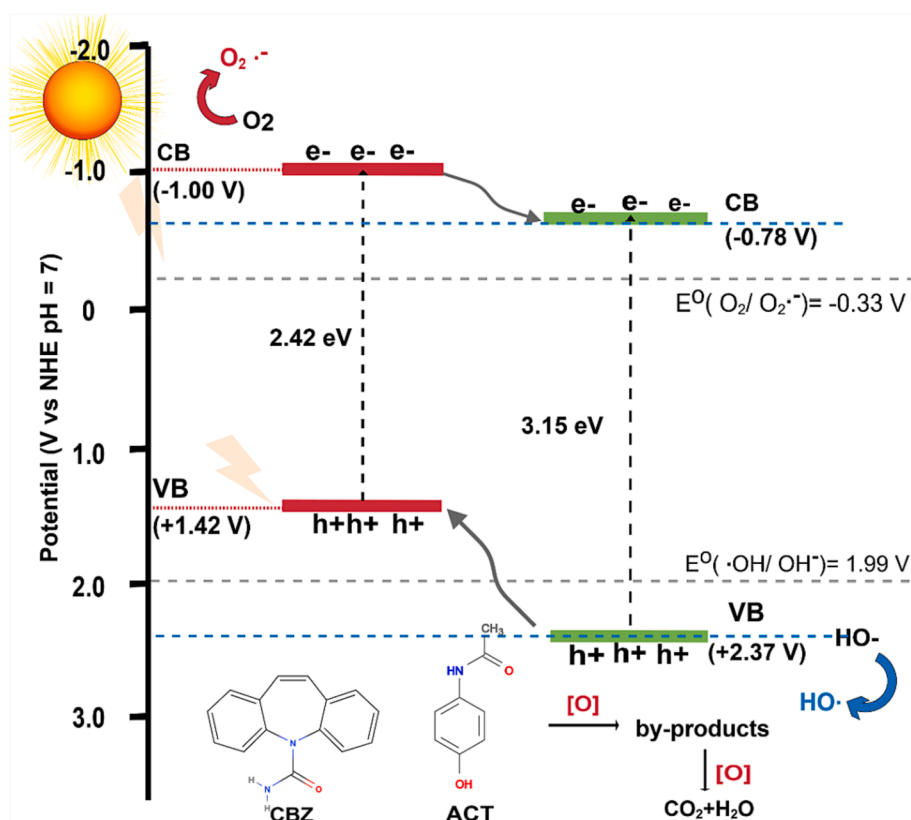


Fig. 18. Schematic illustration of (P,S)-g-C₃N₄/TiO₂ band structure, excitation and photodegradation mechanism of CBZ and ACT under simulated solar light.

aromatic compounds, with -OH substitution at the benzene ring. Noteworthy, the elimination of the acetamide [P7; *m/z* 59.04] from ACT molecule also lead to the possible formation of hydroquinone [P5; *m/z* 110.04] and benzoquinone [P6; *m/z* 108.09] as other by-products. All [P3]-[P7] are expected to break into smaller compounds at the further degradation steps and finally generate CO₂, H₂O and NH₄⁺, as last-step mineralization products. On the other hand, the formation of the dimer [P1] in route (I) is less typical, and analysis of its possible reactivity is less straightforward. In this regard, additional calculations of the Fukui functions for [P1] were performed to possibly identify reactive sites in its molecule. As shown in Fig. 17b, 17c and 17d majority of active sites are located at the aromatic rings of the dimer, both for the electrophilic attack (*f*⁻), radical attack (*f*⁰) and nucleophilic attack (*f*⁺). These results suggest that further degradation of [P1] might occur similarly for the ACT, but with a larger molecule. However, it is also noteworthy that some differences are noticed between *f*⁻ and *f*⁺ maps. Specifically, the electrophilic attack is more probable to occur at the acetamide moiety (atoms N12 and C13 in the Figures), which might lead to the formation of [P2; *m/z* 258.6], as suggested from the MS results. The hydroxyl radicals might especially initiate this transformation since they are electrophilic in nature and were found to be important during the ACT degradation process. On the other hand, the *f*⁺ map clearly shows the preferred site of nucleophilic attack at the dimer-forming bond (C4 and C20 atoms in the Figures), which suggests the hypothetical dissociation of the [P1] back to the smaller molecules is possible as the result of nucleophilic attack. Hypothetically, superoxide radicals might be responsible for such an attack, which might lead to the formation of a product similar to [P3]. This would agree with the observed role of the •O₂⁻ on the process efficiency, however it should be noted that the reactivity of superoxide radicals is generally slower than other reactive species, so this transformation might not be favored.

Furthermore, based on the Mott-Schottky analysis, the flat band potential of (P, S)-g-C₃N₄/TiO₂ (5 %) heterocomposite was determined.

Fig. 18 shows a graphical presentation of the photocatalyst band edges position and charge transfer during excitation with a light greater than its bandgap energy.

The flat band positions of (P, S)-g-C₃N₄ and 2D TiO₂ were calculated to be -1.00 V vs. NHE for (P, S)-g-C₃N₄ and -0.78 V vs. NHE for 2D TiO₂. The valence band edge location was estimated according to a value of the flat band edge position and bandgap energy and amounted to 1.42 V vs. NHE for (P, S)-g-C₃N₄ and 2.37 V vs. NHE for 2D TiO₂. From the photocatalytic mechanism it can be seen that Z-scheme band alignment is formed. Firstly, excited electrons from the valence band (VB) are transferred to the conduction band (CB) and transported onto the photocatalyst surface. The greater photocatalytic activity of (P, S)-g-C₃N₄/TiO₂ nanocomposite compared to 2D TiO₂ and (P, S)-g-C₃N₄ could be attributed to the improved electron transport from (P, S)-g-C₃N₄ to the TiO₂ surface due to the heterojunction formation. Accumulated electrons participate in superoxide anion radicals generation from oxygen as a main reactive oxygen species taking part in the photocatalytic oxidation reaction. Simultaneously, photoinduced holes (h⁺) on the TiO₂ nanosheets are transferred to (P, S)-g-C₃N₄ through efficiently formed heterojunction of (P, S)-g-C₃N₄ and TiO₂. In this way, the recombination of e⁻-h⁺ pairs decreases, and separation efficiency increases, which was confirmed by EIS Nyquist plots analysis as well as emissions and decay times measurements. Since the VB of 2D TiO₂ (2.37 eV) is higher than the standard redox potential of E⁰ (HO⁻/HO[•]) the photoinduced holes can interact with water molecules and produce hydroxyl radicals (HO[•]).

Finally, the reusability tests were performed for pure 2D TiO₂, (P, S)-g-C₃N₄, and the most active composite of (P, S)-g-C₃N₄/TiO₂ (5 %), as presented in Figure S8. The (P, S)-g-C₃N₄/TiO₂ (5 %) showed better stability than (P, S)-g-C₃N₄ and 2D TiO₂. Regarding pharmaceuticals degradation through three consecutive cycles of selected photocatalysts, it was observed that the less stable photocatalyst was (P, S)-g-C₃N₄ with a decline of photocatalytic degradation by 1.54-fold, but the

combination of (P, S)-g-C₃N₄ with 2D TiO₂ generated a more stable photocatalyst. 2D TiO₂ proved to be a more stable photocatalyst with a decline of photocatalytic degradation of 1.18-fold, therefore in the formation of (P, S)-g-C₃N₄/TiO₂ (5 %) contributed to higher stability of heterocomposite.

4. Conclusions

In summary, the novel 2D TiO₂-based hybrid photocatalysts with improved photocatalytic activity were prepared by heterojunction of TiO₂ nanosheets obtained by simple lyophilization method with multi-anion doped g-C₃N₄. The morphological and physicochemical analyses confirmed the formation of Z-scheme heterojunction between (P, S)-g-C₃N₄ and 2D TiO₂, which improved charge carriers separation due to interfacial charge transfer between TiO₂ and (P, S)-doped g-C₃N₄.

The most effective synthesized photocatalyst was composite (P, S)-doped g-C₃N₄/TiO₂ in the optimum loading of 5 % w/w. Phosphorus and sulfur co-doped graphitic carbon nitride contribute to the lower bandgap energy of the formed heterocomposite inhibiting charge carriers recombination. The photoluminescence spectra and carriers lifetime calculations showed better separation of charge carriers in UV light for 2D TiO₂ and under 405 nm excitation (absorption maximum of (P, S)-g-C₃N₄ and sideband of (P, S)-g-C₃N₄/TiO₂ for the composite material. The responsible species for the degradation of pharmaceuticals were superoxide (O₂⁻) and hydroxyl radicals (HO[•]), which contributed to the complete photodegradation of studied pharmaceuticals. For carbamazepine, about 100 % degradation was achieved within 30 min of photodegradation, whereas for acetaminophen, complete removal was observed in 60 min of irradiation. Moreover, the mineralization efficiency measured as TOC values was 76 % for carbamazepine and 40 % for acetaminophen.

A possible mechanism for carbamazepine and acetaminophen photodegradation was proposed over (P, S)-doped g-C₃N₄/ 2D TiO₂ (5 %) photocatalyst, showing dual advantages of increased light-harvesting capacity and efficient charge carriers separation due to heterojunction (P, S)-doped g-C₃N₄ and 2D TiO₂. The optimal (5 %) (P, S)-doped g-C₃N₄/ 2D TiO₂ (5 %) photocatalyst was stable after subsequent cycles of carbamazepine and acetaminophen degradation.

CRedit authorship contribution statement

Elvana Cako: - there is missing of credit authorship of two authors, please add: Grzegorz Trykowski - Formal analysis, Paweł Głuchowski - Formal analysis, Marcin Pisarek - Formal analysis, Data curation, Formal analysis, Investigation, Visualization, Writing - original draft. **Szymon Dudziak**: Data curation, Formal analysis, Investigation, Software, Visualization. **Agnieszka Fiszka Borzyszkowska**: Formal analysis. **Paweł Głuchowski**: Formal analysis. **Grzegorz Trykowski**: Formal analysis. **Marcin Pisarek**: Formal analysis. **Karol Sikora**: Formal analysis. **Anna Zielińska-Jurek**: Conceptualization, Formal analysis, Supervision, Project administration, Funding acquisition, Methodology, Resources, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

The research was financially supported by the Polish National

Science Centre (grant no. NCN 2021/43/B/ST5/02983). Financial support from Gdańsk University of Technology under the Oxygenium program supporting open access publications is acknowledged.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2023.123320>.

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