Visible-light harvesting innovative $W^{6+}/Yb^{3+}/TiO_2$ materials as a green methodology photocatalyst for the photodegradation of pharmaceutical pollutants

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Abstract

In this work, we report on the synthesis of a new-age reusable visible-light photocatalyst using a heterojunction nanocomposite of W^{6+}/Yb^{3+} on a mixed-phase mesoporous network of monolithic TiO_2 . The structural properties of the monolithic photocatalysts are characterized using p-XRD, SEM-EDAX, TEM-SAED, XPS, PLS, UV–Vis-DRS, FT-IR, micro-Raman, TG-DTA, and N_2 isotherm analysis. The electron microscopic analysis reveals a mesoporous network of ordered worm-like monolithic design, with a polycrystalline mixed-phase (anatase/rutile) TiO_2 composite, as indicated by diffraction studies. The UV–Vis-DRS analysis reveals a redshift in the light absorption characteristics of the mixed-phase TiO_2 monolith as a function of W^{6+}/Yb^{3+} co-doping. It is observed that the use of (8.0 mol%) $W^{6+}/0.4$ (mole%) Yb^{3+} co-doped monolithic TiO_2 photocatalyst, with an energy bandgap of 2.77 eV demonstrates superior visible-light photocatalysis, which corroborates with the PLS studies in terms of voluminous e^-/h^+ pair formation. The practical application of the photocatalyst has been investigated through a time-dependent dissipation of enrofloxacin, a widely employed antimicrobial drug, and its degradation pathway has been monitored by LC–MS-ESI and TOC analysis. The impact of physio-chemical parameters such as solution pH, sensitizers, drug concentration, dopant/codopant stoichiometry, catalyst quantity, and light intensity has been comprehensively studied to monitor the process efficiency.

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Graphic abstract

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1 Highlights

- $W^{6+}/Yb^{3+}/TiO_2$ monolith nanocomposite acts as reusable visible-light photocatalyst.
- Photocatalyst reveals a worm-like mesoporous structure with a high surface area.
- Photocatalyst exhibits faster degradation kinetics (0.5 h) for enrofloxacin.
- The monolithic photocatalyst exhibits high durability and reusability character.

2 Introduction

Environmental pollution remains a major challenge in offering a safe environment for human sustainability. The impact imposed by the rampant evolution of pharmaceutically active drugs on the aquatic ecosystem in form of the emergence of drug-resistant bacteria and also the chronic toxic effects induced by pharmaceutical products on various life forms is a matter of debate [1–7]. Fluoroquinolone (FQ) derivatives of antimicrobial drugs are

widely employed as human and veterinary medicines, considering their superior antibacterial properties against a broad range of gram-positive and gram-negative bacteria [8, 9]. In this class, enrofloxacin (commercially known as Baytril), is a common veterinary antibacterial drug that is used for treating infections related to the alimentary tract, respiratory tract, urinary tract, skin, and soft tissues [1, 10]. In addition, it is also used as a feed additive to promote fowl/animal growth in poultry/husbandry farming [11]. However, in general, the administered antibiotics normally undergo partial metabolism and are eventually exposed to the environment either as a parent compound or as a pharmaceutically active by-product. As a result, the discharged drugs and their metabolites pose serious ecological risks in the form of emergence of resistant bacteria, particularly in the aquatic environment, owing to their prolonged exposures [12]. Unfortunately, most of the water treatment techniques such as sedimentation, flocculation, filtration, etc., are ineffective in removing these drugs from the various aquatic systems [13, 14]. Hence, various other treatment processes such as aerobic-anaerobic, electrochemical, and photoelectron-Fenton methods have been exploited [11, 15, 16]. Nonetheless, most of these methods demand the use of highly expensive and

unstable oxidants besides inducing secondary pollutants that find an easy way in contaminating the aquatic environment [17]. Therefore, it's the need of the hour to find an effective methodology that is not only task efficient but also environmentally complaisant.

The current trend for the aqueous removal/dissipation of pharmaceutical drugs is based on advanced oxidation processes (AOPs) [18–21]. Among the various AOPs, heterogeneous photocatalysis has gained considerable attention due to its high efficacy and enduring stability even though it involves the generation of highly reactive hydroxyl and superoxide radicals [22–25]. Moreover, conforming to the low cost and eco-friendly approach, inorganic semiconductor-based photocatalysis has been an encouraging technology for the elimination of organic pollutants from aqueous environment [26–29]. In this line, photoactive materials such as TiO_2 , ZnO , ZnS , CdS , Fe_2O_3 , $\text{g-C}_3\text{N}_4$, etc., have been employed in this process owing to their noted photocatalytic activity [30–33]. Among these, TiO_2 has gained a lot of popularity owing to its non-toxicity, high stability, low cost, and high performance in degrading organic pollutants in presence of water and air [34–38]. But the main drawback with TiO_2 is its energy bandgap (3.2 eV), which confirms its efficiency in the UV region (3–5% of the solar spectra), thus proving its photocatalytic inefficacy in natural sunlight [39]. This eventually tempted the scientific community to think of alternatives that utilizes the excellence of the TiO_2 properties through modified approaches, for visible-light photocatalysis. Many approaches like doping with metallic or non-metallic ions, coupling with small energy bandgap semiconductors, etc., have been established to prepare visible-light-induced photocatalysts [40–43]. Among these, doping with transition metal ions such as iron, copper, tungsten, vanadium, cobalt, molybdenum, manganese, chromium, etc., to increase the efficiency, are quite common [44–53]. Metal ion doping/co-doping process creates new impurity energy levels in the TiO_2 bandgap, thereby causing a redshift that allows visible-light based electronic transitions from the valence band (VB) to the conduction band (CB). The dopant/codopant induced energy levels act as an electron/hole (e^-/h^+) traps, thereby reducing the e^-/h^+ pair recombination rate through the following mechanism.

Here, the energy level for $\text{M}^{n+}/\text{M}^{(n-1)+}$ lies below the conduction band edge (E_{CB}) and the energy level for $\text{M}^{n+}/\text{M}^{(n+1)+}$ stays above the valence band edge (E_{VB}) [54]. The introduction of trap sites not only enhances the

visible-light absorption but also increases the lifetime of photo-induced charge carriers. The metal ions act as recombination sites for the photo-induced charge carriers, thus reducing the quantum yield thereby enhancing the photocatalytic activity of TiO_2 . However, the possible drawbacks associated with transition metal ion doping are the promotion of charge recombination at metal sites and thermal instability. This has been overcome by the co-doping process with rare earth metal ions, which have been proven to increase thermal stability, resist agglomeration and stabilize the mesoporous structures [55, 56]. In this aspect, the geometrical and morphological aspect of the photocatalytic material also plays a key role in the photo-degradation of organic pollutants.

In the recent years, mesoporous monolithic framework has gained a lot of attention, in comparison to nanostructured particles, due to their intriguing structural properties in terms of higher surface area, uniform network, and tunable pore morphologies [57–59]. A variety of mesoporous monolithic templates of TiO_2 are being synthesized recently using ionic, non-ionic surfactants, block polymers, etc., as surfactants i.e. structure-directing agents. Interestingly, the use of mixed-phase titania monolithic composites is prone to show better photocatalytic performance than pristine titania (anatase) due to their synergetic effect, which creates staggered bands thereby inducing e^-/h^+ charge separation and also interfacial electron transfer from rutile to anatase phase [60]. Fuchang Peng et al. prepared a mixed-phase TiO_2 codoped Sm^{3+}/C material for the visible-light photodegradation of methylene blue [61]. Similarly, Zhu Luo et al. designed a V^{4+} doped mixed-phase TiO_2 (61% anatase and 39% rutile) for the visible-light degradation of methylene blue [62]. Hence, it is inferred that with the synergetic advantages of transition and lanthanide metal ions, co-doping of TiO_2 monoliths of high surface area and porosity can increase the performance of the photocatalyst for faster dissipation of pollutants. Therefore, it will be an interesting concept to use mixed-phase mesoporous TiO_2 monolithic composites as heterogeneous photocatalysts for the dissipation of pharmaceutical drugs.

In this work, we report on the synthesis of a novel heterojunction of $\text{W}^{6+}/\text{Yb}^{3+}$ nanocomposite that is integrated with a mixed-phase crystalline mesoporous titania monolith by direct template sol–gel method, using F127 as the structure-directing agent and n-dodecane as the swelling agent, through microemulsion technique. The synthesized mesoporous titania reveals a highly ordered worm-like monolith structure with high surface area and pore volume that exhibits good photocatalytic response under visible-light. To evaluate the photocatalytic efficiency of the proposed photocatalyst, enrofloxacin is used as the model organic pollutant. Besides, we have also performed a comprehensive analytical study to analyze the effect of various physicochemical

parameters such as solution pH, amount of photocatalyst, light intensity, drug concentration, the role of sensitizers, etc., towards the visible-light-induced degradation of enrofloxacin, using the proposed mesoporous monolithic $W^{6+}/Yb^{3+}/TiO_2$ nanocomposite.

3 Experimental

3.1 Chemicals and reagents

All the reagents used for the synthesis of photocatalytically active mesoporous monoliths are procured from Sigma Aldrich and are used without any further purification. Ti(IV) butoxide ($Ti(OBu)_4$) is used as the inorganic precursor of TiO_2 . Chemicals such as WCl_6 and $Yb(NO_3)_3 \cdot 5H_2O$ are used as the dopant and codopant precursors. Pluronic F-127 is used as the structure-directing agent, and n-dodecane is used as the swelling agent, for the synthesis of mesoporous monolithic framework. Enrofloxacin ($C_{19}H_{22}FN_3O_3$) is purchased from CDH chemicals. For solution pH adjustments, a series of 0.2 M buffer solutions of, $ClCH_2COOH-HCl$ (pH 1–3), $CH_3COONa-CH_3COOH$ (pH 4–6), MOPS- $NaOH$ (pH 7–9), and CHES- $NaOH$ (pH 10–11) is used. Deionized water is used for the process of monolith synthesis and photocatalysis studies.

3.2 Instrumentation

A Bruker D8 Advance model powder X-ray diffractometer is used for measuring the wide-angle and low-angle p-XRD pattern, to study the titania monolith phase transitions and porosity, in the range (2θ) of 10° – 90° and 0.2° – 10.0° , respectively. To study the surface morphology and elemental mapping of the monolithic composite, an FEI Quanta FEG 200 model high-resolution scanning electron microscope combined with energy dispersive X-ray spectrometer (HR-SEM-EDAX) is employed. For high-resolution imaging of monolith surface morphology, a Tecnai G2 20 S-Twin model high-resolution transmission electron microscope (HR-TEM) coupled with a small angle electron diffractometer (SAED) has been employed. A Quanta chrome ASiQwin model BET analyzer with an automated gas sorption analyzer is used for surface area (BET) and pore volume (BJH) studies. To study the elemental oxidation states and also the surface composition of the monolithic $W^{6+}/Yb^{3+}/TiO_2$ composite, a PHI 5000 Versa Prob-II model X-ray photoelectron spectrometer (XPS) with monochromatic $Al K\alpha$ radiation (150 W, 15 kV, and 1486.74 eV) is used. To study the e^-/h^+ pair recombination effect, the photoluminescence spectral (PLS) analysis is performed using a Cary Eclipse model spectrofluorometer. The energy bandgap of the photocatalysts are measured using a JASCO V670 model UV–Visible spectrophotometer

with diffused reflectance integrating sphere (DRS). The functional groups associated with the monolith photocatalyst are confirmed using a Thermo Scientific (Nicolet iS10 model) Fourier Transform infrared (FT-IR) spectrophotometer. To study the nature of phase transition, micro-Raman spectral measurements are recorded using a Horiba XploRA Plus model Raman spectrometer, at an excitation wavelength of 532 nm, using an Nd:YAG diode laser. To monitor the thermal stability and hydrophilicity of the monolith, a Seiko SII 7200 model thermogravimetric analyzer (TGA) is used. A Nabertherm (B10-LT5/11 model) muffle furnace is used for the temperature-controlled calcination of the monolithic photocatalyst materials. For the photocatalysis studies, a Heber Scientific (HIPR-MP400 model) annular type photoreactor equipped with tungsten filament lamps (150, 300, and 500 W/cm^2) is employed. The mass fragment data for the photoproducts formed during the photocatalytic degradation of enrofloxacin has been recorded by LC–MS–ESI. The liquid chromatography (LC) is performed on a reverse-phase column (Acquity UPLC BEH C18, 1.7 Micron, 2.1 X 100 mm) using a gradient combination of methanol (LC–MS grade) and water (Milli-Q), as the mobile phase. The mass spectrometric data are acquired using Quattro Premier XE (Micromass MS Technologies), an electrospray ionization (ESI) triple quadrupole mass spectrometer. To study the drug mineralization, an Elementar Vario TOC (cube model) analyzer is used for total organic carbon (TOC) analysis.

3.3 Synthesis of mesoporous monolithic mixed-phase $W^{6+}/Yb^{3+}/TiO_2$ composite

Mesoporous monolithic structured mixed-phase TiO_2 with varying W^{6+}/Yb^{3+} (dopant/codopant) stoichiometry has been synthesized by tri-block copolymer template mediated microemulsion based sol–gel method. For this, a 2.0 g of Pluronic F127 is homogeneously dispersed in 52 mL of deionized water and a 23.3 mL of 2 M HCl is added dropwise, through continuous stirring for 0.5 h. To this homogeneous solution, varying stoichiometry (mole%) of WCl_6 and $Yb(NO_3)_3 \cdot 5H_2O$ are added under constant stirring for 15 min. Further, a 0.5 mL of n-dodecane and 4.0 mL of $Ti(OBu)_4$ are added in sequence, and the mixture is stirred for 6 h, to ensure the complete hydrolysis and condensation of the inorganic precursors to form the desired monolithic framework ($W^{6+}/Yb^{3+}/TiO_2$ composite), as a white gelation. The sol–gel is aged at $40^\circ C$ for 24 h to facilitate the slow evaporation of solvent molecules, thereby eliminating the rapid shrinkage of the monolithic structure, which could potentially rupture the framework. The resulting monolithic gel is calcined at $450^\circ C$ for 6 h at a controlled temperature ramping of $2^\circ C/min$, for the complete removal of inorganic and organic impurities.

3.4 Photocatalysis methodology

The photodegradation efficiency of the synthesized monolithic photocatalyst material is evaluated using specific concentrations of enrofloxacin, under visible-light irradiation in a photoreactor. Based on the optimized working conditions, a suitable quantity of (8.0 mol%) W^{6+} / (0.4 mol%) Yb^{3+} co-doped TiO_2 photocatalyst is equilibrated with a series of enrofloxacin concentrations. To eliminate the background reduction of the target drug (enrofloxacin) concentrations, the drug solutions are equilibrated with the photocatalyst materials under dark for 0.5 h. A 300 W/cm² tungsten lamp is employed as the visible-light source for the irradiation/photo-activation of the synthesized photocatalyst materials. During the irradiation process, a 1.0 mL aliquot of the drug solution is withdrawn at certain time intervals, and are analyzed using a UV–Visible Spectrophotometer at 274 nm (λ_{max}), to monitor the extent of drug degradation. The various physicochemical factors that could potentially influence the process of photocatalytic drug degradation

are systematically studied and optimized by adopting this methodology.

4 Results and discussion

4.1 Characterization of the monolithic photocatalyst

4.1.1 p-XRD analysis

The wide-angle p-XRD pattern for the monolithic photocatalyst composite of varying dopant and codopant ratios are recorded in the range of 10°–90° (2 θ), as depicted in Fig. 1(a, b). The p-XRD pattern confirms the existence of a mixed-phase (rutile and anatase phase) of TiO_2 photocatalyst, where the relative TiO_2 phase ratios depend on the dopant stoichiometry (0–8 mol% W^{6+}). Interestingly, with increasing W^{6+} stoichiometry (0–8 mol%), a considerable decline in the rutile phase peak intensity, along with a reciprocal

Fig. 1 a, b Wide-angle p-XRD patterns, and c low-angle p-XRD patterns for the undoped, W^{6+} doped and W^{6+}/Yb^{3+} co-doped mesoporous TiO_2 monoliths

incline in the anatase phase peak intensity is noticed for monolithic titania. From the JCPDS database, it is comprehended that at 8.0 mol% of W^{6+} doping, the monolithic TiO_2 photocatalyst exhibits a maximum of 80% of photoactive anatase phase and 20% of inactive rutile phase. However, the addition of Yb^{3+} (0–0.8 mol%) as codopant, retains the ratio of rutile and anatase phase composition but has a significant impact on the light absorption characteristics of the photocatalyst. The diffraction peaks at 2θ values of 25.30° (1 0 1), 36.95° (1 0 3), 38.56° (1 1 2), 48.03° (2 0 0), 55.06° (1 0 5), 62.11° (2 1 1), 63.69° (2 1 3), and 68.76° (1 1 6) corresponds to the anatase phase of the TiO_2 composites. Similarly, the 2θ values representing rutile phase in the XRD are 27.43° (1 1 0), 36.07° (1 0 1), 39.18° (2 0 0), 41.23° (1 1 1), 44.04° (2 1 0), 54.31° (2 1 1), 56.62° (2 2 0), 62.75° (0 0 2), 64.04° (3 1 0), 65.50° (3 0 1) and 68.99° (1 1 2). However, no significant XRD peaks are observed for both W^{6+} and Yb^{3+} , which is attributed to their minimal composition with respect to the bulk composition of the TiO_2 network. The relative ratios of anatase to rutile phase in the monolithic framework are established using Spurr-Myer's equation, as indicated below [63].

$$W_R/W_A = 1.22(I_R/I_A) - 0.025$$

Here, I_A and I_R refer to the intensity of anatase (1 0 1) and rutile (1 1 0) reflections, respectively. The crystallite sizes are calculated from the highest intense peaks using the following Scherrer's equation.

$$D = K\lambda/\beta \cos \theta$$

Here, D refers to the crystal size of photocatalyst, K is dimensionless constant, λ is the X-ray wavelength, β is the full-width half maxima (FWHM) of diffraction peaks, and θ is the diffraction angle.

Furthermore, to understand the effect of dopant/codopant ratio (W^{6+}/Yb^{3+}) on the mixed-phase composition of TiO_2 , the d-spacing values for anatase (1 0 1) and rutile (1 1 0) reflections are calculated. With increasing dopant/codopant stoichiometry, a significant variation in the mixed-phase ratio is observed, which is reciprocated through a slight peak shift (2θ) in the anatase (1 0 1) and rutile (1 1 0) reflections, as shown in Fig. 1c. This represents the strong dispersion and bonding properties of the dopant/co-dopant to the TiO_2 framework. Since the ionic radii of W^{6+} (0.640 Å) are smaller than the ionic radii of Ti^{4+} (0.745 Å), it is interpreted that the dopant is intercalated into the TiO_2 framework thus capturing the spaces inside the lattice without dispersing on the surface. Contrarily, the greater ionic radii of Yb^{3+} (0.858 Å) shows a weak surface dispersion on the monolithic TiO_2 framework. The mesoporosity of the monolith is confirmed by low-angle p-XRD (Fig. 1d), with a characteristic

peak at 0.64° (2θ) confirms the uniform arrangement of a mesoporous network within the monolithic framework. This mesoporous structural prodigy eases the accessibility to the active sites for the drug molecules, thereby improving the degradation kinetics.

4.1.2 XPS analysis

The XPS analysis of (8.0 mol%) W^{6+} /(0.4 mol%) Yb^{3+} co-doped TiO_2 monolith is carried out to ascertain the surface elemental state, chemical composition, and ionic state of the prepared monolith. From Fig. 2a, the wide range XPS analysis confirms the elemental presence of Ti, O, W, and Yb, through their corresponding binding energy peaks. The intense $C1s$ peak at 280.83 eV is attributed to the adsorbed carbon impurities in the monolith formed during the calcination process. The high-resolution $Ti2p$ spectra (Fig. 2b) confirms the presence of $Ti2p_{3/2}$ and $Ti2p_{1/2}$ states, with corresponding binding energies at 456.2 eV and 463.8 eV, respectively. This confirms the dominant existence of Ti in the tetravalent (Ti^{4+}) oxidation state in the TiO_2 monolith, which is also supported by the energy difference (Δ 7.6 eV) between the two binding states. The high-resolution spectra in the range of 520–540 eV are analyzed to diagnose the different species of oxygen that are present in the modified TiO_2 monolith, as shown in Fig. 2c. From the spectra, it is addressed that the W^{6+}/Yb^{3+} co-doped TiO_2 possesses two types of oxygen species, one being the lattice oxygen (O_L), which refers to the oxygen atoms in the lattice of the Ti–O–Ti monolith and the other being the surface oxygen (O_S), which refers to the oxygen atoms present on the titania surface as Ti–OH. The high-resolution XPS spectra (Fig. 2d) for W^{6+} reveals two symmetric peaks at 36.9 eV and 34.3 eV that corresponds to $W4f_{5/2}$ and $W4f_{7/2}$ orbital states, respectively, with a Δ value of 2.6 eV that confirms its hexavalent oxidation state [64]. The deconvoluted peaks noticed at 37.4 eV depicts the presence of $Ti3p$ orbital state. [65]. Like-wise, the presence of Yb^{3+} in the monolithic composite is confirmed by the singular peak at 185.3 eV that corresponds to the $Yb4d_{5/2}$ orbital state [66], as indicated in Fig. 2e.

4.1.3 SEM-EDAX and TEM-SAED analysis

The surface morphology of the monolithic photocatalyst are characterized by SEM analysis, and the obtained images are shown in Fig. 3a–e. The HR-SEM images of the W^{6+}/Yb^{3+} co-doped TiO_2 monolith reveals a densely packed framework of single blocks with a well-defined ordered porous network. Further, the SEM images confirms the absence of random aggregation in the monolithic framework and also exposes the roughness in the surface morphology, apart from the existence of a long-range network of mesopores. The EDX spectra for $W^{6+}/Yb^{3+}/TiO_2$ monolith confirms the presence

Fig. 2 XPS survey spectra for **a** 8.0%W⁶⁺/(0.4%)Yb³⁺ co-doped mesoporous TiO₂ monolith, and **b–e** High resolution deconvoluted XPS spectra for Ti2p, O1s, W4f, and Yb4d orbital respectively

of dopant and codopant in the monolithic framework. The elemental composition of the dopant and codopant used for the optimized preparation condition are shown in Fig. 3f. The elemental mapping of all the constituents that are an integral part of the monolithic composite is depicted in Fig. 3g, which unveils the uniform distribution of the dopant and codopant in the TiO₂ framework, without any disordered agglomeration. Furthermore, the existence of a worm-like pattern in the monolithic structure with uniform porosity has been confirmed by HR-TEM images, as illustrated in Fig. 4a–e. The existence of a worm-like monolithic structural network induces favorable conditions for the greater diffusion of the target drug molecules to the photoactive sites, through the porous framework. From the lattice fringes of the HR-TEM imaging, the d-spacing value is calculated as 0.35 nm, which corroborates with the d-spacing data obtained from p-XRD. The SAED pattern (Fig. 4f) for the W⁶⁺/Yb³⁺/TiO₂ monolith supports the existence of a micro-crystalline phase, which further validates the observation from wide-angle p-XRD pattern.

4.1.4 FT-IR, Raman, and TG–DTA plot

Figure 5a shows the FT-IR spectrum for the bare TiO₂, W⁶⁺ doped TiO₂, and W⁶⁺/Yb³⁺ codoped TiO₂ monolith, in the spectral range of 4000–400 cm^{−1}. The broad peaks around

3345 cm^{−1} implicate the symmetrical and asymmetrical stretching frequencies of O–H groups, which could be associated to the surface hydroxyl groups of titania, apart from the adsorbed water molecules. This is further supported by the peak at 1630 cm^{−1} corresponding to the hydroxyl bending vibrational frequency. The strong absorption peak in the range 850–500 cm^{−1} is ascribed to the Ti–O–Ti stretching vibrational modes, thus confirming the formation of a continuous monolithic network. The slight shift in the bare Ti–O vibrational frequency from 533 to 520 cm^{−1} confirms the interaction of the dopant/co-dopant in the form of either lattice intercalation or surface dispersion with the TiO₂ framework [67].

The micro-Raman spectra for the bare TiO₂, W⁶⁺/TiO₂, and W⁶⁺/Yb³⁺/TiO₂ monolith has been recorded to elucidate the nature and type of different combinatorial phases present in the synthesized monolithic materials, which is depicted in Fig. 5b. The anatase phase of TiO₂ is confirmed through the Raman active modes that are observed at 146 cm^{−1} (*E_g*), 395 cm^{−1} (*B_{1g}*), 510 cm^{−1} (*A_{1g}*), and 633 cm^{−1} (*E_g*). Meanwhile, the two intense peaks at 442 cm^{−1} (*E_g*) and 613 cm^{−1} (*A_{1g}*) correspond to the TiO₂ rutile phase vibration modes thus confirming the existence of mixed-phase composition in the bare TiO₂, W⁶⁺ doped TiO₂, and W⁶⁺/Yb³⁺ codoped TiO₂ monolith framework [68]. In the case of W⁶⁺/Yb³⁺ codoped TiO₂ monolithic

Fig. 3 **a–e** HR-SEM images for 8.0%W⁶⁺/(0.4%)Yb³⁺ co-doped TiO₂ monoliths (at various resolutions), **f** EDX analysis for 8.0%W⁶⁺/(0.4%)Yb³⁺ co-doped TiO₂ monolith, and **g** Elemental mapping of Ti⁴⁺, O²⁻, W⁶⁺, and Yb³⁺ ions

composite, with increasing W⁶⁺/Yb³⁺ stoichiometry, a substantial decline in the rutile phase fraction has been noticed, which is in good agreement with the observed p-XRD pattern.

The TGA and DTA curves of the undoped TiO₂ and W⁶⁺/Yb³⁺ co-doped TiO₂ monolith, are shown in Fig. 5c. The TGA pattern for bare and codoped TiO₂ monoliths reveals an initial weight loss of 2.0% and 3.5%, within the temperature range of 60–110 °C, which is attributed to the loss of the adsorbed water molecules that are present in the interstitial pores of the monolithic materials. This also highlights the hydrophilic nature of the photocatalyst in terms of its ability to chemisorb water molecules that can potentially act as carriers for the target drug molecules to the active sites. In this line, a weight loss of about 4.0% is further noticed in the temperature range of 110–450 °C, which is assigned to the thermal decomposition of the inorganic and organic precursors/impurities. However, beyond 450 °C, the weight loss is negligible and the TGA curve shows almost a flat line. The DTA plot also complies with the TGA plot, thereby substantiating the water-retaining capacity and purity of the monolithic materials.

4.1.5 BET/BJH analysis

To determine the surface area and pore size of the monolithic photocatalyst materials, nitrogen adsorption–desorption isotherm analysis has been carried out to calculate the surface area using the BET model, at a relative pressure of 0.01 < p/p₀ < 1.0. Figure 6a shows the isotherm plot for the bare, doped, codoped TiO₂ monolithic materials. The obtained results acknowledge that the surface area for the bare TiO₂, W⁶⁺ (8 mol%) doped TiO₂ and W⁶⁺ (8 mol%)/Yb³⁺ (0.4 mol%) codoped TiO₂ monolith as, 160.41, 127.00, and 77.85 m²/g, respectively, with a corresponding tunable pore volume of 3.21, 3.30 and 17.53 nm. The decrease in the surface area for the W⁶⁺/Yb³⁺/TiO₂ codoped monolith is substratum evidence for the lattice intercalation of W⁶⁺ and surface dispersion Yb³⁺ ions into the monolithic TiO₂ framework. From the isotherm plot, the volume of N₂ gas adsorbed for the W⁶⁺/Yb³⁺/TiO₂ and bare TiO₂ monoliths increases sharply at a relative pressure (p/p) of ~0.8 and 0.6, respectively. The increase in relative pressure for the W⁶⁺/Yb³⁺ codoped TiO₂ monolith can be attenuated to the presence of the dopant (W⁶⁺) and codopant (Yb³⁺) in the

Fig. 4 a–e HR-TEM surface morphology images at different magnifications, and f SAED pattern for 8.0%W⁶⁺/(0.4%)Yb³⁺ co-doped TiO₂ monolith

monolithic framework. However, all the isotherms show a well-defined type-IV isotherm steepness with a characteristic H1 hysteresis loop that conveys the characteristic pattern of a mesoporous worm-like structural network. The BJH pore analysis of the bare, doped, and codoped TiO₂ is depicted in Fig. 6b, which reveals the pore volume for the bare, doped, and codoped TiO₂ as, 0.31, 0.38, and 0.38 cm³/g, respectively. It is inferred that the pore diameter is enhanced by the doping/co-doping process, increasing the effective percolation of the target drug molecules towards the photoactive sites thereby enhancing the photocatalysis kinetics for the dissipation of organic pharmaceutical pollutants using the modified monolithic photocatalyst materials.

4.1.6 UV–Vis-DRS and PLS analysis

The UV – Visible diffuse reflectance spectral measurements are carried out to calculate the energy bandgap (E_g), for bare TiO₂, W⁶⁺ doped TiO₂, and W⁶⁺/Yb³⁺ codoped TiO₂ monolith, as depicted in Fig. 7a. The bandgap calculations are performed using the Kubelka–Munk function, which is followed by the extrapolation of the Tauc's plot, using the following equation.

$$\alpha h\nu = A(h\nu - E_g)^n$$

Here, 'A' is a dimensionless constant, 'n' is 0.5 that corresponds to the indirect transitions, 'h' is Planck's constant, ' ν ' is the frequency of the light, and ' α ' is the attenuation constant.

The energy bandgap for the bare TiO₂, W⁶⁺ (8 mol%) doped TiO₂ and W⁶⁺ (8 mol%)/ Yb³⁺ (0.4 mol%) codoped TiO₂ monolith are calculated to be 3.27, 2.99 and 2.77 eV, respectively. It is noticed that a redshift phenomenon is observed for the W⁶⁺ doped TiO₂ and Yb³⁺ codoped TiO₂ monoliths, with respect to the bare TiO₂ monolith. This change in the light adsorption phenomena is attributed to the introduction of dopant/codopant into the TiO₂ framework that results in the effective orbital interaction with the energy levels of TiO₂. This efficiently narrows the energy gap lowering the e^-/h^+ recombination rate thereby promoting visible-light-induced photocatalysis. The doping/co-doping process creates new Fermi energy levels between the valence and conduction band of TiO₂. The narrowed energy bandgap from the doping/co-doping process is attributed to the charge transfer occurring within the VB/CB states of TiO₂, and also with the intermediate energy states of dopant/co-dopant. It is inferred that the lattice intercalated dopant (W⁶⁺) forms an intermediate energy state and the surface bounded co-dopant (Yb³⁺) with an unpaired electronic state further helps in the bandgap narrowing by forming a new paired energy level in TiO₂. This intermediate energy state also helps in trapping the e^-/h^+ thereby reducing the recombination of e^-/h^+ pairs.

Fig. 5 **a** FT-IR spectra, and **b** micro-Raman spectra for undoped, W⁶⁺ doped and W⁶⁺/Yb³⁺ co-doped TiO₂ monoliths, and **c** TG–DTA pattern for undoped and 8.0%W⁶⁺/(0.4%)Yb³⁺ co-doped TiO₂ monoliths

It is well known that the e⁻/h⁺ recombination is responsible for photoluminescence phenomena and the intensity of photoluminescence spectra directly depends on the rate of e⁻/h⁺ recombination. Hence, it can be inferred that the intensity of the PL spectra for a photocatalyst is inversely proportional to its photocatalytic activity. Figure 7b, c shows the PL spectra for different stoichiometric ratios of, W⁶⁺ doped and Yb³⁺ codoped TiO₂, respectively, with respect to bare TiO₂ monolith at an excitation wavelength of 300 nm. The decrease in peak intensity at 361 nm upon increasing dopant and codopant content until the threshold level is a clear evidence for the decrease in the e⁻/h⁺ recombination effect and a subsequent increase in the photocatalytic efficiency of the monolithic composite. The high intensity PLS observed for the bare TiO₂

monolith is due to the large bandgap between VB and CB states, which promotes e⁻/h⁺ recombination. However, with increasing W⁶⁺ doping the inter-energy states reduce the bandgap, thereby acting as e⁻ and h⁺ trap sites that eventually reduces the extent of e⁻/h⁺ pair recombination. From the doping process, the use of 8.0 mol% W⁶⁺ doped TiO₂ monolith offered the least PL intensity, with a maximum photocatalytic efficiency. Like-wise, the co-doping process with increasing Yb³⁺ content up to 0.4 mol% also reflected in the gradual decrease in the PL intensity, for the 8.0 mol% W⁶⁺ doped TiO₂ monolithic material. Based on the PLS data, it is confirmed that the use of W⁶⁺ (8.0 mol%)/ Yb³⁺ (0.4 mol%) codoped TiO₂ monolithic photocatalyst showed the best photocatalytic performance under visible-light illumination.

Fig. 6 **a** N₂ adsorption–desorption isotherm (BET analysis), and **b** BJH pore size distribution for undoped, W⁶⁺ doped and W⁶⁺/Yb³⁺ co-doped TiO₂ monoliths

4.2 Mechanism of visible-light photocatalysis

The monolithic structure of the proposed photocatalyst not only provides a larger surface area but offers a uniformly distributed mesoporous worm-like structural patterns. The unique structural features that are associated with the monolith photocatalyst facilitates an easy and voluminous interaction of the target pollutant molecules with the photocatalyst reactive sites, for the eventual photocatalytic degradation. The mesopore framework enhances the photon-induced e⁻/h⁺ charge separation process by rapidly diffusing the quanta produced during the photocatalytic reaction and eventually transporting the photogenerated charges for the formation of reactive radical intermediate species, thereby reducing the recombination rate of e⁻/h⁺ pairs.

In the case of W⁶⁺/Yb³⁺ co-doped TiO₂ monolith, it is noticed that the stoichiometric infusion of W⁶⁺ and Yb³⁺, along with the presence of a mixed-phase TiO₂ (1:5, rutile/anatase) has significantly contributed towards the enhancement in the e⁻/h⁺ pair separation process. The lower band energy states of the W⁶⁺/Yb³⁺ codopant allows the electrons to escape easily to the monolithic surface to form reactive radical species for photodegradation. As reported earlier, the bandgap of the rutile phase is lower than that of the anatase phase (3.03 and 3.2 eV), and the synergetic effect between the two phases creates a staggered band gap thereby promoting the charge separation. However, the migration of charges across the phase junction remains a mystery but it is commonly agreed that the electrons proceed from the rutile phase to the anatase

phase and the holes migrate from the anatase phase to the rutile phase. It is understood that the photo-excited electrons move from the VB to the CB state of the rutile phase through the narrowed energy bandgap that is induced by the codoped W⁶⁺/Yb³⁺ energy states. Eventually, the photo-excited electrons migrate to the lower energy CB of the anatase phase of TiO₂ through the phase junction and subsequently interacts with the surface molecular oxygen surface to form superoxide radicals. Contrastingly, the photogenerated holes proceed from the lower energy of the VB anatase phase to the higher energy VB state rutile phase of TiO₂ to generate extremely reactive hydroxyl radicals by interaction with the surface hydroxyl molecules [62]. These radical intermediates subsequently react with the target molecules to degrade them into photoproducts through a series of photochemical reactions, as shown in Scheme 1. The extent of light-induced photocatalytic drug degradation into less harmful photoproducts that are eventually mineralized in the aquatic environment has been studied by LC–MS/MS–ESI. A possible degradation pathway for the enrofloxacin drug through the process of photocatalysis has been represented in Scheme 2.

4.3 Optimization of analytical parameters for photocatalytic efficacy

4.3.1 Solution pH

The efficacy in the process of photocatalytic degradation of enrofloxacin can sequentially be analyzed by varying the pH

Fig. 7 **a** UV-Vis-DRS plot, and **b, c** PL spectra for different mole ratio of W^{6+} doped and W^{6+}/Yb^{3+} co-doped TiO_2 monoliths

conditions of the aqueous medium, as depicted in Fig. 8a. From the photodegradation profile of enrofloxacin solution, it is evident that at pH 3.0, the kinetics of drug dissipation is at its maximum. This behavior at pH 3.0, is attributed to the maximum interaction of the enrofloxacin molecule (i.e., 1-cyclopropyl-7-(4-ethyl-1-piperazinyl)-6-fluoro-1,4-dihydro-4-oxo-3-quinoline carboxylic acid) with the protonated ($TiOH_2^+$) photocatalyst surface. The accumulation of protons on the TiO_2 surface gravitates the photocatalyst material to act as a cationic species ($TiOH_2^+$), thereby inducing an electrostatic interaction with the electron-rich centers of enrofloxacin molecules. Moreover, the cation ($TiOH_2^+$) state at the TiO_2 surface induces electrostatic attractive propulsion for the water molecules that act as carriers for the drug molecules thereby increasing the proximity and availability of these drug molecules in the TiO_2 lattice. The prominent water-retaining capacity of the monolithic photocatalyst helps in enhancing the rate of hydroxyl radical

(OH $\cdot$) generation upon visible-light illumination, thereby promoting faster degradation kinetics of the adsorbed drug molecules on the TiO_2 framework. However, under alkaline or neutral pH conditions, the prominent presence of anionic (TiO^-) state of the TiO_2 surface creates a repulsive force of interaction with the hydrated drug molecules. This incongruity decreases the photocatalysis efficiency of the photocatalyst materials in terms of drug dissipation kinetics. Moreover, the influential presence of hydroxyl (OH $^-$) species under these conditions results in the production of hydroxyperoxy ions (HOO $^-$) with the dissolved oxygen thereby reducing the effective generation of reactive radical intermediates.

4.3.2 Dosage of photocatalyst material

The dosage of photocatalyst required for the photocatalytic process is one of the key parameters, as it significantly

Scheme 1 Graphical representation of the visible-light light-induced photocatalytic mechanism for W^{6+}/Yb^{3+} co-doped TiO_2 monoliths, for enrofloxacin degradation

influences the process efficiency and also the kinetics. To explore this parameter, a series of drug solutions (15 ppm) that are maintained at a solution pH of 3.0 are individually equilibrated with varying dosages (25–200 mg) of 8.0% W^{6+} /0.4% Yb^{3+} co-doped TiO_2 monolithic photocatalyst prior to visible-light (300 W/cm^2) illumination. Figure 8b shows that the photocatalytic drug degradation kinetics increases significantly up to the usage of 100 mg of photocatalyst. This behavior is attributed to the greater availability of photoactive sites with an increase in the amount of catalyst that eventually enhances the formation of hydroxyl and superoxide radicals, for enrofloxacin degradation. However, with > 100 mg of photocatalyst, there is a significant decline in the drug degradation kinetics due to the excess availability/dispersion of the photocatalyst materials, thereby hindering the effective light penetration through the solution bulk. This eventually hampers the interaction of photons with the photocatalyst materials that are present at the lower section of the solution bulk, thereby inhibiting the formation of reactive radicals thus causing a decline in the degradation rate. Hence, from the observed analytical results, it can be inferred that the use of 100 mg of the photocatalyst is ambient for the complete dissipation of 15 ppm of drug solution at an optimized solution pH of 3.0.

4.3.3 Drug concentration

The effect of drug concentration plays a vital role in ascertaining the kinetics factor involved in the enrofloxacin drug degradation with respect to the optimized monolithic photocatalyst dosage. For this experiment, the photodegradation kinetics studies have been executed by irradiating varying concentrations of drug solutions (5–25 ppm), under optimized experimental conditions for a specific time duration (2 h). From Fig. 8c, it is inferred that the rate of drug dissipation exhibits first-order degradation kinetics. It is observed that the rate of drug degradation depends on its concentration and with increasing concentration of enrofloxacin from 5 to 15 ppm the process efficiency did not show any significant change. This can be ascribed to the structural properties of the photocatalyst in terms of high surface area and pore volume (in comparison to nanoparticulate composites) that serves as the gateway for greater adsorption of enrofloxacin drug molecules onto the catalytic active sites of $W^{6+}/Yb^{3+}/TiO_2$ monolithic composite. However, a decrease in the drug degradation efficiency is noticed beyond 15 ppm, which is attributed to the near saturation in the number of photoactive sites that are available in the monolithic composite (100 mg), in hosting higher drug concentrations. Moreover, the excess drug molecules that are dispersed in the aqueous solution

Scheme 2 Schematic representation of the photoproducts identified through LC–MS/MS–ESI, for the visible-light photocatalytic degradation of enrofloxacin under optimized experimental conditions

could potentially mask the active sites of the photocatalyst from interaction with the dissolved O_2 , to create reactive radicals during the process of light irradiation. Besides, the other possible reason for the decline in the drug degradation kinetics can be ascertained to the partial absorption of the incident photons by the non-adsorbed (solution dispersed) drug molecules thereby reducing the net available photons to interact and activate the catalytic reactive sites of the monolithic composite.

4.3.4 Role of sensitizers

Photosensitizers are electron acceptors that are usually deployed to accelerate the process of photodegradation. In heterogeneous photocatalysis, most of the metal oxide/sulfide based photocatalysts are associated with low quantum yield due to e^-/h^+ pair recombination effect. The use of photosensitizers as electron acceptors promptly generates highly reactive radicals ($O_2^{\cdot-}$ and $OH^{\cdot}$), thus reducing the

Fig. 8 Effect of, **a** solution pH, **b** amount of catalyst, **c** drug concentration, **d**, **e** photosensitizers, and **f** light intensity, on enrofloxacin drug degradation

chance of e^-/h^+ pair recombination. In the present study, despite the superior degradation kinetics exhibited by the $W^{6+}/Yb^{3+}/TiO_2$ composite, the role of photosensitizers has been tested to monitor any further enhancement in the degradation kinetics, as indicated in fig. 8d, e. For this study, common photosensitizers such as H_2O_2 , $(CH_3)_2CO$, $KBrO_3$, and humic acid (HA) of varying concentrations are employed to study the photocatalytic degradation kinetics of enrofloxacin, in the presence of $W^{6+}/Yb^{3+}/TiO_2$ monolith, under visible-light irradiation. The order of activity of the deployed photosensitizers towards enrofloxacin degradation kinetics are as follows, $HA > H_2O_2 > KBrO_3 > (CH_3)_2CO$. In the case of acetone, the sensitization starts with the generation of excited $(CH_3)_2CO$ molecules by the photoexcitation processes followed by a secondary chemical energy transfer from the excited acetone molecules to the drug molecules. However, at higher acetone concentrations, this secondary photochemical process ensures the internal quenching of the excited acetone molecules, thereby diminishing the effectiveness of the drug degradation process. In the case of $KBrO_3$, the electron capturing efficiency is significantly improved, thereby reducing the e^-/h^+ pair recombination effect. In the case of H_2O_2 , it reacts with superoxide radicals to form several hydroxyl radicals thereby enhancing the drug degradation process. However, beyond a threshold

limit of H_2O_2 (> 1.0 mM), the drug degradation kinetics is not effective due to the h^+ scavenging properties of the hydroxyl radicals. However, in the presence of humic acid (a high molecular mass of phenolic and carboxylic acid units) due to the presence of diverse active sites that results in the voluminous generation of active species, there is a significant promotion in the drug degradation kinetics. Based on the sensitizer studies, $> 98\%$ drug degradation is observed within 0.5 h of visible-light irradiation (300 W/cm^2), with 10 ppm of humic acid, at a solution pH of 3.0, using 100 mg of photocatalyst material.

4.3.5 Light intensity

The intensity of the incident light primarily determines the number of quanta of photons interacting with the photocatalytic material. To have a better understanding, different light intensities (150, 300, and 500 W/cm^2) of tungsten filament lamps are used as the visible-light source for the photocatalytic drug degradation studies, as indicated in Fig. 8f. From the obtained results, it is evident that the use of a low-intensity lamp (150 W/cm^2) yields only 64% degradation within a time frame of 0.5 h, under the optimized drug concentration (15 ppm) using 100 mg of photocatalyst material at a solution pH of 3.0, in the presence of 10 ppm

of humic acid (sensitizer). However, with 300 and 500 W/cm² light intensities, a superior degradation of > 98% is observed within 0.5 h of illumination. This shows that the light intensity of the visible-light source has a direct effect on the drug degradation kinetics due to the increased availability of quanta of photons that eventually increases the generation of e⁻/h⁺ pairs by interacting with active sites of the photocatalyst material that carries suitable dopant/co-dopant stoichiometry. It is noticed that despite the enhanced rate of drug degradation with 500 W/cm² light intensity, the large amount of heat generated during the irradiation process makes it objectionable to be used for a prolonged period, considering the high chances of thermal pollution. Thus, the use of 300 W/cm² light intensity has been considered optimal for the photocatalytic studies.

4.3.6 TOC and reusability plot

To monitor the extent of mineralization of the enrofloxacin molecules during the process of visible-light-induced photocatalysis, a known aliquot of the photolysis samples is subjected to TOC analysis, to study the total organic content as a function of time, as shown in Fig. 9a. The TOC plot reveals an exponential decrease in the total organic content of the drug samples as a function of irradiation time. In the

case of the W⁶⁺/Yb³⁺ co-doped TiO₂ monolith photocatalyst, the residual TOC is found to be ≤ 1.5 ppm within 0.5 h of irradiation that gradually reduces to ≤ 0.02 ppm after 2 h of photocatalysis, using optimized experimental conditions in the presence of sensitizers (10 ppm of HA). Interestingly, the comparison of the TOC plot with the photodegradation kinetics plot reveals a relatively different picture of the extent of drug degradation and eventually mineralization. For an illumination time of 0.5 h nearly ≥ 99% of drug molecules are photodegraded in the kinetics plot but the extent of drug mineralization is ≤ 90%, as revealed by the TOC plot. This can be attributed to the fact that the drug molecules degrade into various photoproducts that are having a relatively high persistence in the aqueous solution, thus leading us to infer that for completion drug mineralization, an irradiation period of 2 h, is necessary. This prolonged period is due to the degradation of enrofloxacin into simple organic molecules followed by their effective mineralization to CO₂ and H₂O.

To understand the durability and reusability properties of the monolithic photocatalyst materials, along with their analytical data reproducibility character, the photocatalysis studies are carried out for five repeated cycles, under optimized experimental conditions, as shown in Fig. 9b. The reusability plot reveals that the synthesized monolithic photocatalyst

Fig. 9 **a** TOC plot for enrofloxacin drug, and **b** Reusability studies of 8.0%W⁶⁺/(0.4%)Yb³⁺ co-doped TiO₂ monoliths towards enrofloxacin degradation

Table 1 Comparison of photocatalytic efficiency of the proposed work with respect to enrofloxacin drug degradation literature reports

S. no	Photocatalyst	Light source	Degradation kinetics	Catalyst amount (mg)	Drug conc. (ppm)	Ref.
1	Polyacrylic acid-grafted-carboxylic graphene/titanium nanotube	Visible (150 W/cm ² , Xe)	90 min	100	4	[69]
2	Graphene-like BN modified BiPO ₄ material	UV lamp	120 min	30	10	[70]
3	Graphene-WO ₃ nanocomposites	Pulsed Discharge Plasma	60 min	200	20	[71]
4	Ag ₂ O/CeO ₂ Heterojunction material	Visible (300 W/cm ² , Xe)	120 min	50	10	[72]
5	Multifunctional Fe ₃ O ₄ @TiO ₂ -GO composite	Visible (500 W/cm ² , Xe)	240 min	20	2	[73]
7	Ordered mesoporous g-C ₃ N ₄ material	Visible (350 W/cm ² , Xe)	50 min	1000	17	[74]
8	Magnetic imprinted TiO ₂ photocatalyst	Visible (300 W/cm ² , W)	90 min	100	20	[75]
9	Mesoporous W ⁶⁺ /Yb ³⁺ co-doped TiO ₂ Monolith	Visible (300 W/cm ² , W)	30 min	100	15	Present Work

did not reveal any loss in its photocatalysis efficiency, for the dissipation of the target pollutants, even after five cycles of usage. It is to note that the studies performed related to photocatalyst reusability and data reproducibility are impractical with nanoparticulate based photocatalyst materials that are reported in the literature. Here, the use of a novel photocatalyst composite particularly in the form of mesoporous monolithic structures is the main reason behind such diverse utility. The superior performance of the proposed monolithic photocatalyst has been compared with photocatalyst materials that are reported in the literature [69–75], and the observation are tabulated in Table 1.

5 Conclusion

To summarize, we report a first of its kind novel W⁶⁺/Yb³⁺ co-doped mesoporous TiO₂ monolithic photocatalyst material that has been synthesized using surface direct directing tri-block copolymer mediated microemulsion based sol–gel technique. The surface morphology and structural features of the monolithic photocatalyst have been characterized using various structural and surface characterization techniques. The UV–Vis-DRS data revealed a narrowed energy band gap of 2.77 eV for the W⁶⁺ (8.0 mol%)/ Yb³⁺ (0.4 mol%) codoped TiO₂ composite, thereby reflecting on its visible-light photocatalytic activity, which has been tested using enrofloxacin, as the target organic pollutant. The p-XRD data confirmed the existence of a mixed-phase TiO₂ crystallinity and the high-resolution microscopic images confirmed the uniform mesoporous pattern with an ordered worm-like framework for the monolithic composites. The BET and BJH analysis reflected on the high surface area and pore properties of the monolithic photocatalysts that eventually transformed into effective drug adsorption and faster light-induced degradation kinetics. The oxidation states of the monolithic composite have been confirmed by XPS, which

also concurred with the lattice and surface dispersion characteristics of the W⁶⁺ and Yb³⁺, respectively, on the TiO₂ lattice framework. The photocatalytic efficacy of the mixed-phase TiO₂ mesoporous monolithic materials revealed that a maximum drug degradation efficiency under visible-light irradiation (300 W/cm²) can be achieved within a time of 0.5 h, using 100 mg of photocatalyst material for a drug solution (15 ppm) of pH 3.0, in the presence of 10 ppm of humic acid. This superior analytical performance of the synthesized monolithic photocatalyst reflects on its practical application in water purification and environmental remediation.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. Yan, W., Zhang, J., & Jing, C. (2016). Enrofloxacin transformation on shewanella oneidensis MR-1 reduced goethite during anaerobic-aerobic transition. *Environmental Science and Technology*. <https://doi.org/10.1021/acs.est.6b03054>
2. Gao, J., Huang, J., Chen, W., Wang, B., Wang, Y., Deng, S., & Yu, G. (2016). Fate and removal of typical pharmaceutical and personal care products in a wastewater treatment plant from Beijing: a mass balance study. *Frontiers of Environmental Science and Engineering*. <https://doi.org/10.1007/s11783-016-0837-y>
3. Michael, I., Rizzo, L., McArdell, C. S., Manaia, C. M., Merlin, C., Schwartz, T., Dagot, C., & Fatta-Kassinos, D. (2013). Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review. *Water Research*. <https://doi.org/10.1016/j.watres.2012.11.027>

4. Zhao, W., Guo, Y., Lu, S., Yan, P., & Sui, Q. (2016). Recent advances in pharmaceuticals and personal care products in the surface water and sediments in China. *Frontiers of Environmental Science and Engineering*. <https://doi.org/10.1007/s11783-016-0868-4>
5. Hirsch, R., Ternes, T., Haberer, K., & Kratz, K. L. (1999). Occurrence of antibiotics in the aquatic environment. *Science of the Total Environment*. [https://doi.org/10.1016/S0048-9697\(98\)00337-4](https://doi.org/10.1016/S0048-9697(98)00337-4)
6. Ji, Y., Ferronato, C., Salvador, A., Yang, X., & Chovelon, J. M. (2014). Degradation of ciprofloxacin and sulfamethoxazole by ferrous-activated persulfate: Implications for remediation of groundwater contaminated by antibiotics. *Science of the Total Environment*. <https://doi.org/10.1016/j.scitotenv.2013.11.008>
7. Li, N., Tang, S., Rao, Y., Qi, J., Zhang, Q., & Yuan, D. (2019). Peroxymonosulfate enhanced antibiotic removal and synchronous electricity generation in a photocatalytic fuel cell. *Electrochimica Acta*, 298, 59–69. <https://doi.org/10.1016/j.electacta.2018.12.063>
8. Fakhri, A., Behrouz, S., & Pourmand, M. (2015). Synthesis, photocatalytic and antimicrobial properties of SnO_2 , SnS_2 and $\text{SnO}_2/\text{SnS}_2$ nanostructure. *Journal of Photochemistry and Photobiology B: Biology*. <https://doi.org/10.1016/j.jphotobiol.2015.05.017>
9. Fink, L., Dror, I., & Berkowitz, B. (2012). Enrofloxacin oxidative degradation facilitated by metal oxide nanoparticles. *Chemosphere*. <https://doi.org/10.1016/j.chemosphere.2011.10.002>
10. Jia, A., Wan, Y., Xiao, Y., & Hu, J. (2012). Occurrence and fate of quinolone and fluoroquinolone antibiotics in a municipal sewage treatment plant. *Water Research*. <https://doi.org/10.1016/j.watres.2011.10.055>
11. Guinea, E., Garrido, J. A., Rodríguez, R. M., Cabot, P. L., Arias, C., Centellas, F., & Brillas, E. (2010). Degradation of the fluoroquinolone enrofloxacin by electrochemical advanced oxidation processes based on hydrogen peroxide electrogeneration. *Electrochimica Acta*. <https://doi.org/10.1016/j.electacta.2009.11.040>
12. Sturini, M., Speltini, A., Maraschi, F., Profumo, A., Pretali, L., Fasani, E., & Albini, A. (2010). Photochemical degradation of marbofloxacin and enrofloxacin in natural waters. *Environmental Science and Technology*. <https://doi.org/10.1021/es100278n>
13. Zhao, C., Zhou, Y., de Ridder, D. J., Zhai, J., Wei, Y., & Deng, H. (2014). Advantages of $\text{TiO}_2/\text{5A}$ composite catalyst for photocatalytic degradation of antibiotic oxytetracycline in aqueous solution: Comparison between TiO_2 and $\text{TiO}_2/\text{5A}$ composite system. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2014.03.050>
14. Arikian, O. A. (2008). Degradation and metabolization of chlortetracycline during the anaerobic digestion of manure from medicated calves. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2008.01.096>
15. Wang, C., Yin, L., Xu, Z., Niu, J., & Hou, L. A. (2017). Electrochemical degradation of enrofloxacin by lead dioxide anode: Kinetics, mechanism and toxicity evaluation. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2017.06.038>
16. dos Santos, A. B., Cervantes, F. J., & van Lier, J. B. (2007). Review paper on current technologies for decolourisation of textile wastewaters: Perspectives for anaerobic biotechnology. *Biore-source Technology*. <https://doi.org/10.1016/j.biortech.2006.11.013>
17. Zada, A., Qu, Y., Ali, S., Sun, N., Lu, H., Yan, R., Zhang, X., & Jing, L. (2018). Improved visible light activities for degrading pollutants on $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposites by decorating SPR Au nanoparticles and 2,4-dichlorophenol decomposition path. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2017.09.005>
18. Klauson, D., Babkina, J., Stepanova, K., Krichevskaya, M., & Preis, S. (2010). Aqueous photocatalytic oxidation of amoxicillin. *Catalysis Today*. <https://doi.org/10.1016/j.cattod.2010.01.015>
19. Palominos, R., Freer, J., Mondaca, M. A., & Mansilla, H. D. (2008). Evidence for hole participation during the photocatalytic oxidation of the antibiotic flumequine. *Journal of Photochemistry and Photobiology A: Chemistry*. <https://doi.org/10.1016/j.jphotochem.2007.06.017>
20. Akhundi, A., Badiei, A., Ziarani, G. M., Habibi, Y. A., Muñoz, M. M. J., & Luque, R. (2020). Graphitic carbon nitride-based photocatalysts: Toward efficient organic transformation for value-added chemicals production. *Molecular Catalysis*. <https://doi.org/10.1016/j.mcat.2020.110902>
21. Habibi, Y. A., Asadzadeh, K. S., Feizpoor, S., & Rouhi, A. (2020). Review on heterogeneous photocatalytic disinfection of waterborne, airborne, and foodborne viruses: Can we win against pathogenic viruses? *Journal of Colloid and Interface Science*. <https://doi.org/10.1016/j.jcis.2020.07.047>
22. Chen, P., Wang, F., Chen, Z. F., Zhang, Q., Su, Y., Shen, L., Yao, K., Liu, Y., Cai, Z., Lv, W., & Liu, G. (2017). Study on the photocatalytic mechanism and detoxicity of gemfibrozil by a sunlight-driven TiO_2 /carbon dots photocatalyst: The significant roles of reactive oxygen species. *Applied Catalysis B: Environmental*. <https://doi.org/10.1016/j.apcatb.2016.11.040>
23. Sayed, M., Ismail, M., Khan, S., Tabassum, S., & Khan, H. M. (2016). Degradation of ciprofloxacin in water by advanced oxidation process: Kinetics study, influencing parameters and degradation pathways. *Environmental Technology (United Kingdom)*. <https://doi.org/10.1080/09593330.2015.1075597>
24. Akhundi, A., Habibi, Y. A., Abitorabi, M., & Rahim, P. S. (2019). Review on photocatalytic conversion of carbon dioxide to value-added compounds and renewable fuels by graphitic carbon nitride-based photocatalysts. *Catalysis Reviews—Science and Engineering*. <https://doi.org/10.1080/01614940.2019.1654224>
25. Habibi, Y. A., Feizpoor, S., Seifzadeh, D., & Ghosh, S. (2020). Improving visible-light-induced photocatalytic ability of TiO_2 through coupling with $\text{Bi}_2\text{O}_3/\text{Cl}$ and carbon dot nanoparticles. *Separation and Purification Technology*. <https://doi.org/10.1016/j.seppur.2019.116404>
26. Mahlambi, M. M., Ngila, C. J., & Mamba, B. B. (2015). Recent developments in environmental photocatalytic degradation of organic pollutants: the case of titanium dioxide nanoparticles: A review. *Journal of Nanomaterials*. <https://doi.org/10.1155/2015/790173>
27. Wang, W. K., Chen, J. J., Li, W. W., Pei, D. N., Zhang, X., & Yu, H. Q. (2015). Synthesis of Pt-loaded self-interpersed anatase TiO_2 with a large fraction of (001) facets for efficient photocatalytic nitrobenzene degradation. *ACS Applied Materials and Interfaces*. <https://doi.org/10.1021/acsami.5b06161>
28. Sedaghati, N., Habibi, Y. A., Pirhashemi, M., Asadzadeh, K. S., & Ghosh, S. (2020). Integration of BiOI and Ag_3PO_4 nanoparticles onto oxygen vacancy rich- TiO_2 for efficient visible-light photocatalytic decontaminations. *Journal of Photochemistry and Photobiology A: Chemistry*. <https://doi.org/10.1016/j.jphotochem.2020.112659>
29. Pirhashemi, M., Habibi, Y. A., & Rahim, P. S. (2018). Review on the criteria anticipated for the fabrication of highly efficient ZnO -based visible-light-driven photocatalysts. *Journal of Industrial and Engineering Chemistry*. <https://doi.org/10.1016/j.jiec.2018.01.012>
30. Lin, C. C., & Chiang, Y. J. (2012). Feasibility of using a rotating packed bed in preparing coupled ZnO/SnO_2 photocatalysts. *Journal of Industrial and Engineering Chemistry*. <https://doi.org/10.1016/j.jiec.2011.11.152>
31. Zhang, Y., Zhang, N., Tang, Z. R., & Xu, Y. J. (2012). Graphene transforms wide band gap ZnS to a visible light photocatalyst. The new role of graphene as a macromolecular photosensitizer. *ACS Nano*. <https://doi.org/10.1021/nn304154s>

32. Sabri, M., Habibi, Y. A., Chand, H., & Krishnan, V. (2020). Activation of persulfate by novel TiO₂/FeOCl photocatalyst under visible light: Facile synthesis and high photocatalytic performance. *Separation and Purification Technology*. <https://doi.org/10.1016/j.seppur.2020.117268>
33. Asadzadeh, K. S., & Habibi, Y. A. (2020). g-C₃N₄/carbon dot-based nanocomposites serve as efficacious photocatalysts for environmental purification and energy generation: A review. *Journal of Cleaner Production*. <https://doi.org/10.1016/j.jclepro.2020.124319>
34. Naraginti, S., Thejaswini, T.V.L., Prabhakaran, D., Sivakumar, A., Satyanarayana, V.S.V., & ArunPrasad, A.S. (2015). Enhanced photo-catalytic activity of Sr and Ag co-doped TiO₂ nanoparticles for the degradation of Direct Green-6 and Reactive Blue-160 under UV & visible light. *Spectrochimica Acta—Part A Molecular and Biomolecular Spectroscopy*. Doi: <https://doi.org/10.1016/j.saa.2015.04.101>
35. Liu, B., Khare, A., & Aydil, E. S. (2011). TiO₂-B/anatase core-shell heterojunction nanowires for photocatalysis. *ACS Applied Materials and Interfaces*. <https://doi.org/10.1021/am201123u>
36. Sun, H., Wang, S., Ang, H. M., Tadé, M. O., & Li, Q. (2010). Halogen element modified titanium dioxide for visible light photocatalysis. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2010.05.069>
37. Huang, L. H., Sun, C., & Liu, Y. L. (2007). Pt/N-codoped TiO₂ nanotubes and its photocatalytic activity under visible light. *Applied Surface Science*. <https://doi.org/10.1016/j.apsusc.2007.02.048>
38. Shekofteh, G. M., Habibi, Y. A., Abitorabi, M., & Rouhi, A. (2018). Magnetically separable nanocomposites based on ZnO and their applications in photocatalytic processes: A review. *Critical Reviews in Environmental Science and Technology*. <https://doi.org/10.1080/10643389.2018.1487227>
39. Dong, H., Zeng, G., Tang, L., Fan, C., Zhang, C., He, X., & He, Y. (2015). An overview on limitations of TiO₂ based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. *Water Research*. <https://doi.org/10.1016/j.watres.2015.04.038>
40. Zhang, J., Xi, J., & Ji, Z. (2012). Mo+N Codoped TiO₂ sheets with dominant 001 facets for enhancing visible light photocatalytic activity. *Journal of Materials Chemistry*. <https://doi.org/10.1039/c2jm32391e>
41. Lv, X. J., Zhou, S. X., Zhang, C., Chang, H. X., Chen, Y., & Fu, W. F. (2012). Synergetic effect of Cu and graphene as cocatalyst on TiO₂ for enhanced photocatalytic hydrogen evolution from solar water splitting. *Journal of Materials Chemistry*. <https://doi.org/10.1039/c2jm33325b>
42. Anpo, M., & Takeuchi, M. (2003). The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation. *Journal of Catalysis*. [https://doi.org/10.1016/S0021-9517\(02\)00104-5](https://doi.org/10.1016/S0021-9517(02)00104-5)
43. Legrini, O., Oliveros, E., & Braun, A. M. (1993). Photochemical Processes for Water Treatment. *Chemical Reviews*. <https://doi.org/10.1021/cr00018a003>
44. Deng, Q. R., Xia, X. H., Guo, M. L., Gao, Y., & Shao, G. (2011). Mn-doped TiO₂ nanopowders with remarkable visible light photocatalytic activity. *Materials Letters*. <https://doi.org/10.1016/j.matlet.2011.04.010>
45. Hamal, D. B., & Klabunde, K. J. (2011). Valence state and catalytic role of cobalt ions in cobalt TiO₂ nanoparticle photocatalysts for acetaldehyde degradation under visible light. *Journal of Physical Chemistry C*. <https://doi.org/10.1021/jp200405y>
46. Sathishkumar, P., Anandan, S., Maruthamuthu, P., Swaminathan, T., Zhou, M., & Ashokkumar, M. (2011). Synthesis of Fe³⁺ doped TiO₂ photocatalysts for the visible assisted degradation of an azo dye. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. <https://doi.org/10.1016/j.colsurfa.2010.12.022>
47. Štengl, V., & Bakardjieva, S. (2010). Molybdenum-doped anatase and its extraordinary photocatalytic activity in the degradation of Orange II in the UV and vis regions. *Journal of Physical Chemistry C*. <https://doi.org/10.1021/jp104271q>
48. Liu, B., Wang, X., Cai, G., Wen, L., Song, Y., & Zhao, X. (2009). Low temperature fabrication of V-doped TiO₂ nanoparticles, structure and photocatalytic studies. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2009.04.068>
49. Mazille, F., Schoettl, T., & Pulgarin, C. (2009). Synergistic effect of TiO₂ and iron oxide supported on fluorocarbon films. Part 1: Effect of preparation parameters on photocatalytic degradation of organic pollutant at neutral pH. *Applied Catalysis B: Environmental*. <https://doi.org/10.1016/j.apcatb.2009.01.027>
50. Couselo, N., García Einschlag, F. S., Candal, R. J., & Jobbágy, M. (2008). Tungsten-doped TiO₂ vs pure TiO₂ photocatalysts: Effects on photobleaching kinetics and mechanism. *Journal of Physical Chemistry C*. <https://doi.org/10.1021/jp0769781>
51. Zhu, J., Deng, Z., Chen, F., Zhang, J., Chen, H., Anpo, M., Huang, J., & Zhang, L. (2006). Hydrothermal doping method for preparation of Cr³⁺-TiO₂ photocatalysts with concentration gradient distribution of Cr³⁺. *Applied Catalysis B: Environmental*. <https://doi.org/10.1016/j.apcatb.2005.08.013>
52. Colón, G., Maicu, M., Hidalgo, M. C., & Navío, J. A. (2006). Cu-doped TiO₂ systems with improved photocatalytic activity. *Applied Catalysis B: Environmental*. <https://doi.org/10.1016/j.apcatb.2006.03.019>
53. Klosek, S., & Raftery, D. (2002). Visible light driven V-doped TiO₂ photocatalyst and its photooxidation of ethanol. *Journal of Physical Chemistry B*. <https://doi.org/10.1021/jp004295e>
54. Choi, W., Termin, A., & Hoffmann, M. R. (1994). The role of metal ion dopants in quantum-sized TiO₂: Correlation between photoreactivity and charge carrier recombination dynamics. *Journal of Physical Chemistry*. <https://doi.org/10.1021/j100102a038>
55. Zhang, Y., Zhang, H., Xu, Y., & Wang, Y. (2004). Significant effect of lanthanide doping on the texture and properties of nanocrystalline mesoporous TiO₂. *Journal of Solid State Chemistry*. <https://doi.org/10.1016/j.jssc.2004.05.026>
56. Li, F. B., Li, X. Z., & Hou, M. F. (2004). Photocatalytic degradation of 2-mercaptobenzothiazole in aqueous La³⁺-TiO₂ suspension for odor control. *Applied Catalysis B: Environmental*. <https://doi.org/10.1016/j.apcatb.2003.10.003>
57. Ortel, E., Sokolov, S., Zielke, C., Lauermann, I., Selve, S., Weh, K., Paul, B., Polte, J., & Kraehnert, R. (2012). Supported mesoporous and hierarchical porous Pd/TiO₂ catalytic coatings with controlled particle size and pore structure. *Chemistry of Materials*. <https://doi.org/10.1021/cm301081w>
58. Armelao, L., Barreca, D., Bottaro, G., Gasparotto, A., Tondello, E., Ferroni, M., & Polizzi, S. (2004). Au/TiO₂ nanosystems: A combined RF-sputtering/sol-gel approach. *Chemistry of Materials*. <https://doi.org/10.1021/cm0353308>
59. Antonelli, D. M., & Ying, J. Y. (1995). Synthesis of hexagonally packed mesoporous TiO₂ by a modified Sol-Gel method. *Angewandte Chemie International Edition in English*. <https://doi.org/10.1002/anie.199520141>
60. Liu, Z., Zhang, X., Nishimoto, S., Jin, M., Tryk, D. A., Murakami, T., & Fujishima, A. (2007). Anatase TiO₂ nanoparticles on rutile TiO₂ nanorods: A heterogeneous nanostructure via layer-by-layer assembly. *Langmuir*. <https://doi.org/10.1021/la7018023>
61. Peng, F., Gao, H., Zhang, G., Zhu, Z., Zhang, J., & Liu, Q. (2017). Synergistic effects of Sm and C co-doped mixed phase crystalline TiO₂ for visible light photocatalytic activity. *Materials*. <https://doi.org/10.3390/ma10020209>
62. Luo, Z., Poyraz, A. S., Kuo, C. H., Miao, R., Meng, Y., Chen, S. Y., Jiang, T., Wenos, C., & Suib, S. L. (2015). Crystalline mixed

- phase (anatase/rutile) mesoporous titanium dioxides for visible light photocatalytic activity. *Chemistry of Materials*. <https://doi.org/10.1021/cm5035112>
63. Spurr, R. A., & Myers, H. (1957). Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer. *Analytical Chemistry*. <https://doi.org/10.1021/ac60125a006>
 64. Ruggieri, F., Di Camillo, D., Maccarone, L., Santucci, S., & Lozzi, L. (2013). Electrospun Cu-, W- and Fe-doped TiO₂ nanofibres for photocatalytic degradation of rhodamine 6G. *Journal of Nanoparticle Research*. <https://doi.org/10.1007/s11051-013-1982-x>
 65. Jiang, X., Li, C., Liu, S., Zhang, F., You, F., & Yao, C. (2017). The synthesis and characterization of ytterbium-doped TiO₂ hollow spheres with enhanced visible light photocatalytic activity. *RSC Advances*. <https://doi.org/10.1039/c7ra02165h>
 66. Liu, X., Pan, K., Wang, L., Dong, C., Xiao, X., & Wang, Y. (2015). Butane detection: W-doped TiO₂ nanoparticles for a butane gas sensor with high sensitivity and fast response/recovery. *RSC Advances*. <https://doi.org/10.1039/c5ra20886f>
 67. Kumaresan, L., Prabhu, A., Palanichamy, M., Arumugam, E., & Murugesan, V. (2011). Synthesis and characterization of Zr⁴⁺, La³⁺ and Ce³⁺ doped mesoporous TiO₂: Evaluation of their photocatalytic activity. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2010.11.124>
 68. Wang, W. K., Chen, J. J., Zhang, X., Huang, Y. X., Li, W. W., & Yu, H. Q. (2016). Self-induced synthesis of phase-junction TiO₂ with a tailored rutile to anatase ratio below phase transition temperature. *Scientific Reports*. <https://doi.org/10.1038/srep20491>
 69. Anirudhan, T. S., Shainy, F., & Christa, J. (2017). Synthesis and characterization of polyacrylic acid- grafted-carboxylic graphene/ titanium nanotube composite for the effective removal of enrofloxacin from aqueous solutions: Adsorption and photocatalytic degradation studies. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2016.09.073>
 70. Chen, Z., Chen, X., Di, J., Liu, Y., Yin, S., Xia, J., & Li, H. (2017). Graphene-like boron nitride modified bismuth phosphate materials for boosting photocatalytic degradation of enrofloxacin. *Journal of Colloid and Interface Science*. <https://doi.org/10.1016/j.jcis.2016.12.050>
 71. Guo, H., Jiang, N., Wang, H., Lu, N., Shang, K., Li, J., & Wu, Y. (2019). Pulsed discharge plasma assisted with graphene-WO₃ nanocomposites for synergistic degradation of antibiotic enrofloxacin in water. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2019.04.119>
 72. Wen, X. J., Niu, C. G., Zhang, L., Liang, C., & Zeng, G. M. (2018). A novel Ag₂O/CeO₂ heterojunction photocatalysts for photocatalytic degradation of enrofloxacin: possible degradation pathways, mineralization activity and an in depth mechanism insight. *Applied Catalysis B: Environmental*. <https://doi.org/10.1016/j.apcatb.2017.09.060>
 73. Yu, Y., Yan, L., Cheng, J., & Jing, C. (2017). Mechanistic insights into TiO₂ thickness in Fe₃O₄@TiO₂-GO composites for enrofloxacin photodegradation. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2017.05.092>
 74. Wang, F., Feng, Y., Chen, P., Wang, Y., Su, Y., Zhang, Q., Zeng, Y., Xie, Z., Liu, H., Liu, Y., Lv, W., & Liu, G. (2018). Photocatalytic degradation of fluoroquinolone antibiotics using ordered mesoporous g-C₃N₄ under simulated sunlight irradiation: Kinetics, mechanism, and antibacterial activity elimination. *Applied Catalysis B: Environmental*. <https://doi.org/10.1016/j.apcatb.2018.01.024>
 75. Lu, Z., Chen, F., He, M., Song, M., Ma, Z., Shi, W., Yan, Y., Lan, J., Li, F., & Xiao, P. (2014). Microwave synthesis of a novel magnetic imprinted TiO₂ photocatalyst with excellent transparency for selective photodegradation of enrofloxacin hydrochloride residues solution. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2014.03.077>