



Wireless pulsed nanophotoelectrochemical cell for the ultrafast degradation of organic pollutants

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ABSTRACT

An urgent demand exists for advanced-technologies to efficiently remove persistent organic pollutants from water, while minimizing energy consumption. Here, we introduce an innovative wireless nanophotoelectrochemical (nPEC) cell using pulsed light for the ultrafast degradation/mineralization of organic pollutants. The nPEC cell comprises a nanostructured Si-pn photodiode that monolithically integrates: (i) a Si-n/Au nanowire-based-photocathode for effective light absorption and photovoltage generation, and (ii) a Si-p/mesoporous-NiPt photoanode serving as catalyst to wirelessly amplify the sulfate radical production by low-intensity light without any bias voltage. The efficacy of the nPEC cell was shown by ultrafast degradation (>99 %) and mineralization (>98 %) of three emerging pollutants (tetracycline, levofloxacin and anatoxin-A). Notably, reaction kinetics were boosted by more than one order of magnitude when exposed to light intensities ca. 5-fold lower than sunlight. Remarkably, pulsed light beams in the 100–500 Hz range provided an additional enhancement in the degradation/mineralization efficiencies, reducing energy-input by half, while enhancing the catalyst's oxidation state and durability.

1. Introduction

Various traditional methods can be applied to remove contaminants from water to ensure safe and clean drinking water, including biological treatment, flocculation, sedimentation, adsorption, membrane filtration, or chemical treatments [1–4]. However, conventional methods are often insufficient to effectively eliminate emerging organic pollutants due to their low concentrations. Note that some cyanotoxins can have harmful effects even at levels as low as parts per billion (ppb) [5,6].

Advanced oxidation processes (AOPs) are a promising solution for eliminating contaminants, especially at concentrations in the range of parts per million or even lower. AOPs operate via radical-mediated mechanisms to break down – or even mineralize (i.e., total oxidation) – complex organic compounds into harmless byproducts that can be utilized by living organisms [7–9]. The generation of these radicals is a

critical factor in chemical and photochemical reactions that can occur through various mechanisms, enabling a broad range of chemical transformations. One mechanism to form radicals is electron transfer, in which a catalyst enhances the charge exchange with the species, allowing the generated radical to participate in the chemical reactions [10,11]. Consequently, optimizing radical-mediated mineralization requires meticulous consideration of both the radical initiator and the environmental conditions to ensure the highest possible yield of radicals [12–14].

Peroxymonosulfate (PMS) is an effective oxidizing agent that can produce highly reactive radicals under specific conditions. Typically, oxidized compounds of transition metals such as Fe, Co, Mn, or Ni are used as reducing agents to activate PMS [15–18]. Upon interaction with the reducing agent, PMS undergoes a series of reactions leading to the formation of highly reactive sulfate radicals (SO₄•⁻). The sulfate radical,

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which has high redox potential (2.6–3.1 V), can be used for various chemical and environmental applications, including oxidation and conversion of organic contaminants into harmless carbon dioxide and water [19,20]. Notably, sulfate radicals offer advantages over the hydroxyl radicals, including effective operation across a broader pH range and longer lifespan. As a result, sulfate radical-based oxidation processes have gained increasing attention for environmental remediation due to their high reactivity and ability to oxidize a broad group of toxic and non-biodegradable emerging organic pollutants [20,21]. However, there is still a need to find new PMS activation methods that maximize the generation of sulfate radicals in a simple and cost-effective way, to improve the degradation efficiency of organic pollutants.

Photoelectrochemical (PEC) oxidation is another advanced oxidation process, which can overcome the limitations associated with photocatalysis (e.g., electron-hole recombination) and conventional electrocatalysis [22–26]. In PEC cells, photons generate photocarriers, which are efficiently separated via an applied bias potential. However, in the case of photoelectrochemical oxidation, both light and applied potential are employed to generate strong oxidants that indiscriminately oxidize the organic compounds in wastewater. Despite the potential of PEC cells, current research efforts primarily focus on other processes, such as water splitting [27–29]. In this context, the development of new PEC cells enabling wireless operation (without application of any bias voltage) could greatly simplify the reactors and their operational cost, offering interesting applications for environmental remediation.

Here, we demonstrate the first nanophotoelectrochemical (nPEC) cell enabling wireless amplification of the generation of sulfate radicals from PMS, to achieve ultrafast degradation and mineralization of three different persistent organic pollutants (tetracycline, levofloxacin and anatoxin-A) with low energy consumption. The nPEC cell monolithically integrates a Si pn photodiode featuring a nanostructured Si-n/Au photocathode and a Si-p/mesoporous-NiPt photoanode. The Ni-rich NiPt alloy was selected due to its capacity to form highly stable mesoporous networks via simple electrodeposition techniques, providing an extremely high surface area of oxidized Ni, which is ideal for the PMS activation. The combination of this layer with the nanostructured Si photodiode, which is optimized to enhance the light absorption in the near infrared, enables the light induced modulation of the surface charges in the mesoporous NiPt layer, thus enhancing the electrostatic interaction with the charged species in the solution. As a result, the nPEC cell drastically amplifies the PMS activation and the generation of sulfate radicals with low intensity near infrared light without any external wiring or application of bias voltage. Strikingly, we demonstrate that illumination with a pulsed light beam with a frequency in the 100–500 Hz range enables an additional amplification of the pollutant degradation efficiency, despite the 2-fold reduction of the average light intensity and, therefore, total input energy. The wireless nPEC cells with pulsed illumination open the path to the mineralization of organic pollutants with very high energy efficiency.

2. Experimental details

2.1. Fabrication and characterization of the wireless nanophotoelectrochemical cell

The fabrication of the nPEC cells on 4" p-doped silicon wafers (single side polished, resistivity 1 Ohm-cm) started with the implantation of phosphorous as n-dopant by a ion implanter EATON NV4206 (energy 50 KeV, density $4 \cdot 10^{15} \text{ cm}^{-2}$), followed by diffusion and activation of the dopants via thermal oxidation process (Tempress Furnace, TS-Series V) under atmospheric pressure. This process generated a built-in pn junction at a depth of 500 nm. Next, the Ti (1 nm) and Au (75 nm) layers were deposited at both sides of the Si wafer by e-beam evaporation (OERLIKON UNIVEX 450B). To enable an efficient light absorption and photovoltage generation at low light intensity, the photo-active side of the wafer with the pn-junction was nanopatterned by low cost and

scalable colloidal nanolithography on the whole wafer surface. The Au surface on the n-doped region was activated by oxygen reactive ion etching (RIE, Alcatel AMS 110 DE) (HF 100 W, 30 sccm, 3 Pa) and amide-functionalized polystyrene beads (diameters ca. 200 nm, Thermo Fisher Scientific) were self-assembled on the whole 4" Au surface by incubation the beads colloidal dispersion at 0.1 % during 3 min. This was followed by thorough rinsing with deionized water and drying with N₂ airflow, yielding a randomly distributed monolayer of polystyrene spheres on the Au surface, which was used as mask to fabricate the Si-n/Au nanowires by a two-step RIE process. First, Ar RIE (ICP 1000 W, HF 50 W, 20 sccm, 1 Pa, 2 min, Alcatel AMS 110 DE) was used to etch the Au layer and leave Au discs under the polystyrene beads. Second, SF₆/C₄F₈ RIE (ICP 800 W, HF 15 W, SF₆ 150 sccm, C₄F₈ 100 sccm, 2.7 Pa, 40 s, Alcatel AMS 110 DE) formed the Si/Au nanowires with a height of around 460 nm. The leftovers of the polystyrene beads on the Si/Au nanowires were mechanically removed by a clean-room adhesive tape. The wafers were then cut into 7 mm x 14 mm chips to proceed with the electrodeposition of the mesoporous NiPt layer on the p-doped side of the Si wafer using the deposited Au layer as electrode.

The Ni-rich mesoporous NiPt deposits were potentiostatically electrodeposited with an Autolab PGSTAT30 equipment and the NOVA software. The electrochemical depositions were performed in a thermostated three-electrode system using Ag|AgCl|Cl⁻ as the reference electrode and a platinum spiral as the counter-electrode. The electrochemical media was a block copolymer micellar solution composed of Na₂PtCl₆ (3 mM – Sigma-Aldrich, 98 %), NiCl₂ (200 mM – Sigma-Aldrich, 98 %), H₃BO₃ (200 mM – Sigma-Aldrich, >99.5 %), NH₄Cl (25 mM – Sigma-Aldrich, >99.5 %), and 10 g L⁻¹ of the block copolymer poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol), Pluronic P-123 (Sigma-Aldrich, average M_n ~ 5800). The pH was adjusted to 2.7 by adding HCl (Sigma-Aldrich, 37 %) to the solution. Before the experiments, solutions were deaerated with argon and maintained in an argon atmosphere during the electrochemical experiments. The temperature was kept at 30 °C [30,31].

The morphology of the Au/Si pillar and the porous NiPt deposits was examined with field-emission scanning microscopy (FE-SEM; JSM-7100F Analytical Microscope). The elemental composition of the NiPt deposits was determined by using coupled energy-dispersive spectroscopy (EDS) at 20 kV, calibrated using pure cobalt standard, and by inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer Optima 3200 RL) after dissolving the NiPt layer using 4 % nitric acid. Before and after the catalytic experiments, the chemical nature of NiPt deposits were further examined with X-ray photoelectron spectroscopy (XPS) in an ultra-high vacuum chamber with an XPS system (PHI 5600 MultiTechnique, Physical Electronics) using a monochromatic X-ray source (Al K_α line = 1486.6 eV, 350 W).

The optoelectrical measurements were performed on a custom-made 2-electrode set up. The nPECL cells were sealed in a well, with the bottom Ni/Pt surface acting a working electrode and a Pt wire as counter electrode. A water solution containing the same PMS (OXONE®, Sigma-Aldrich) concentration as the degradation experiments (0.3 mM) contacting only the optically active nanostructured Si/Au surface was used during the measurements. The samples were illuminated with a collimated fiber coupled LED sources with emission at 810 nm (Thorlabs M810F2) or white light (Thorlabs MWWHF2). The light intensity was controlled and pulsed with a LED controller (Thorlabs DC2200). The photovoltages were directly detected with a National Instruments data acquisition card (NI-6352) and processed with a Labview program. The photocurrents were measured with a transimpedance I/V amplifier (Thorlabs PDA200C).

2.2. Pollutant degradation experiments

Single-pollutant solutions of tetracycline (20 ppm – Sigma-Aldrich, >99.5 %), levofloxacin (20 ppm – Sigma-Aldrich, 98.0 %), and (±)-anatoxin-A fumarate (5 ppm – Hello Bio Limited, > 99 %) at a pH of

7.0 were used to investigate the potential of the wireless nanophotocatalytic cell. Degradation and mineralization experiments were performed in a 3 mL quartz cuvette at 20 °C (see Fig. S1).

Firstly, the persistence of the three contaminants in aqueous solution at a pH of 7 was analyzed over a period of 7 days without any actuation. Measurements of time-dependent UV-vis spectra and by high-performance liquid chromatography mass-spectroscopy (HPLC) chromatograms as well as the total organic content (TOC) values demonstrated the persistence of the contaminants and, thus, the maintained harmful potential of all three species.

In a typical degradation experiment, the catalyst was immersed in the pollutant solution for 3 min to achieve adsorption-desorption equilibrium. The solution was magnetically stirred throughout the process. Afterward, 0.3 mL of 3 mM PMS solution was added to the cuvette.

In addition, the impact of sodium chloride, sodium bromide, sodium fluoride, ammonium fluoride, sodium bicarbonate, sodium nitrate, and sodium phosphate, each at a concentration of 10 mM, on the degradation and mineralization of tetracycline was also studied under dark and infrared light illumination conditions.

A UV-vis spectrophotometer (UV-vis, UV-1800 Shimadzu) was used to measure the concentration of tetracycline and levofloxacin at different reaction times and under different irradiation conditions. In addition, tetracycline, levofloxacin and anatoxin-A concentrations were also determined by high-performance liquid chromatography mass-spectroscopy (HPLC-MS, Waters Xevo G2-XS QToF system). The mobile phase comprised a 0.1 % (v/v) formic acid (Sigma-Aldrich, >98 %) aqueous solution, with elution at a flow rate of 0.2 mL min⁻¹ and an injected volume of 2 µL. A linear gradient elution transitioned from 90 % formic acid aqueous solution and 10 % acetonitrile (Sigma-Aldrich, >99.9 %) to a final composition of 10 % formic acid aqueous solution and 90 % acetonitrile over 4 min. Mass-spectroscopy analysis was performed using an electrospray ionization source in positive ion mode (capillary voltage: 4.0 kV; N₂ gas flow rate; gas temperature: 300 °C). The concentration of anatoxin-A at different times was determined using an ultra-high-performance liquid chromatography (UHPLC) system (Accela; Thermo Fisher Scientific) and a Kinetex HILIC column (Phenomenex) with a 100 mm × 2.1 mm inner diameter and particles 2.6 µm in size. A gradient elution solvent based on solvent A (i.e., 95 % [v/v] of acetonitrile and 5 % [v/v] 2 mM of ammonium formate (Sigma-Aldrich, >99.0 %) + 3.6 mM of formic acid aqueous solution) and solvent B (i.e., 2 mM of ammonium formate + 3.6 mM of formic acid aqueous solution) was used. The UHPLC system was coupled to a triple quadrupole mass spectrometer (TSQ Quantum Ultra AM, Thermo Fisher Scientific) equipped with a heated electrospray ionization source (HESI-1). The Xcalibur software (version 2.0; Thermo Fisher Scientific) was used to control the LC-MS system and to process the data. Mineralization was examined by determining the total organic content (TOC) in the aqueous solution (TOC-VCSH, Shimadzu). The different irradiation conditions were applied using the collimated fiber coupled LED source with emission at 810 nm or white light controlled and pulsed with the LED controller.

2.3. Determination of the concentration of sulfate and hydroxyl radicals

A sensitive spectrophotometric method was used to determine the concentration of sulfate and hydroxyl radicals. The relative concentration of sulfate radicals was indirectly evaluated by quantifying Ce(IV) through UV-spectrophotometry, after the reaction between sulfate radicals and Ce(III). In these experiments, the nPEC cell was immersed in a solution containing 3 mL of 10 mM Ce₂(SO₄)₃ and 0.3 mL of 3 mM PMS at pH 7.0. The maximum absorbance of the formed Ce(IV) at $\lambda = 320$ nm was determined at different time intervals over 30 min in the dark and under continuous and pulsed light irradiation. The concentration of sulfate radicals was determined using a calibration curve with known concentrations of Ce(IV) sulfate [32].

To further confirm the PMS decomposition via a radical process, the remaining concentration of non-activated PMS after the interaction with the nPEC cell in the absence of pollutants was determined by iodometry. In a standard experiment, 3 mL of the reaction medium that was in contact with the nPEC cell under different conditions (dark, continuous light, and pulsed light irradiation) was mixed with 1.0 g of KI (Sigma-Aldrich, >99.0 %) and magnetically stirred for 30 min. This promoted the reaction between the PMS and the iodide ions, and the concentration of the triiodide ion was followed through UV-Vis spectroscopy, quantifying the absorption peak at 352 nm. The concentration of the triiodide ion was proportional to the concentration of non-activated PMS after the interaction with the nPEC cell [32,33].

The concentration of hydroxyl radicals was measured by the time-dependent decrease of the fluorescence peak of the fluorescein sodium salt – Sigma-Aldrich – (8 µM, emission at 515 nm and excitation at 303 nm) in an aqueous solution. In a typical experiment, the nPEC cell was immersed in 3 mL of 8 µM fluorescein sodium salt aqueous solution in the absence and presence of PMS (0.3 mL of 3 mM of PMS) at pH = 7.0. The experiments were performed in the dark and under continuous and pulsed light irradiation. To determine the concentration of the fluorescein sodium salt and its rate, a calibration curve was necessary. This involved comparing the unknown concentration to a set of standard samples with known concentrations. The fluorescence emission and excitation spectra were measured using an AMINCO-Bowman Series 2 spectrofluorometer with a quartz micro-cell at 25 °C [34–36].

3. Results and discussion

3.1. Characterization of the wireless nanophotocatalytic cell

Fig. 1 shows the schematic of the wireless nanophotocatalytic (nPEC) cell, which integrates two differentiated functional parts: (i) the light active side with a pn-junction, in which the n doped layer is formed by an array of Si/Au nanowires (NW) homogeneously distributed across the surface (average diameter and height 270 nm and 460 nm, respectively, surface density of 12 NW µm⁻², gold nanodiscs thickness 70 nm) acting as photocathode, and (ii) the catalytically active layer on the p-doped Si side, acting as photoanode, formed by a Ni-rich mesoporous NiPt film.

The fabrication nPEC cells was carried out following the following steps: (i) implantation and activation of the n dopants on the polished side of 4-inch p-doped Si wafers, (ii) deposition of Au layers (75 nm) on both sides of the wafers, (iii) large scale colloidal nanolithography on the implanted n-doped side to form the Si/Au nanowires in the whole wafer surface (Fig. 1b), (iv) wafer dicing in chips of 7 mm x 14 mm, and (v) deposition of the catalytic mesoporous NiPt film (between 130 µg and 160 µg per nPEC cell) on the p-doped side of the chips (Fig. 1c) via a simple potentiostatic block-copolymer templated electrodeposition process, in which the block-copolymer micelles acted as porogen agents (more details can be found in the experimental section).

The nanostructured light-active side containing the pn-junction was designed to maximize the absorption of the NIR radiation (wavelength 810 nm) used in this work, and to maximize the generated photovoltages. The enhanced light absorption is due to the excitation of hybrid plasmonic/dielectric resonances in the Si/Au nanowires [37]. Note that the spectral position of the pure plasmonic resonance of the Au nanodiscs is located over 1.5 µm wavelength. This light active side was able to generate open circuit photovoltages up to 500 mV, for a continuous wave light intensity of ca. 50 mW·cm⁻² (Fig. 1d). The photovoltage versus intensity curve exhibited an initial steep increase for light intensities up to 4 mW·cm⁻², and slower increment over this intensity. In contrast, for pulsed light illumination with a square shape pattern, the photovoltage showed a square-shape pattern with an initial sharp increase and slower decrease when the light intensity was turned to zero (Fig. 1e). In the case of 100 Hz square modulation, the photovoltage was able to drop up to zero before the next light pulse was on.

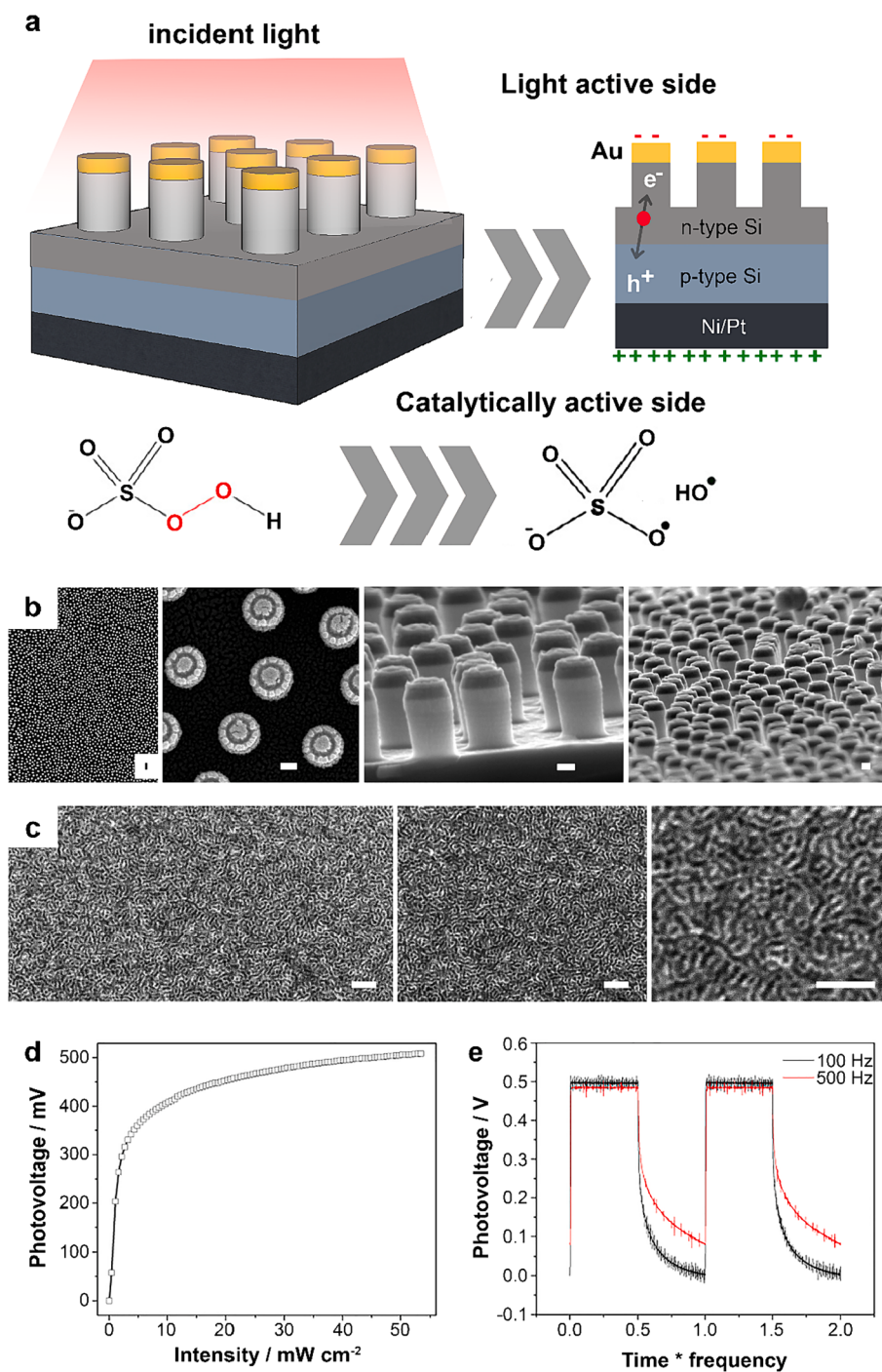


Fig. 1. Wireless nanophotoelectrochemical cell. a) Schematic illustration of the wireless nanophotoelectrochemical cell and the working principle. b) FE-SEM images of the arrays of Au/Si nanowires in the n doped side of the wafer. c) Mesoporous NiPt films prepared at -1000 mV on the unpolished p doped side of the wafer. Scale bars: 100 nm; d) Generated photovoltages vs light intensity for continuous wave light beam, and e) Photovoltage changes under squared-pulsed light with 100 Hz and 500 Hz frequencies, under a light intensity of $50 \text{ mW} \cdot \text{cm}^{-2}$.

However, the nPEC cell, which acts as a capacitor, was not able to fully discharge when the square-pulsed light had a frequency of 500 Hz. Therefore, in this case, an average higher photovoltage could be obtained compared to the 100 Hz light modulation, which had an important effect on the opto-electric amplification of the catalytic effects, as will be shown below.

On the other hand, the catalytically active mesoporous Ni-rich NiPt layer (Fig. 1c) was designed to merge the high catalytic efficiency of Ni oxides and the very high surface area that can be obtained with the NiPt alloys, to maximize the transformation of peroxymonosulfate (PMS) into

highly reactive sulfate and hydroxyl radicals in the absence of illumination. The morphology and composition were fine-tuned by selecting the applied potential [30,38]. Table S1 summarizes the elemental composition of each electrodeposit as a function of the applied potential. The nickel content increased as the applied potential became more negative, but the quality of the porosity and the film thickness diminished. Therefore, a compromise between nickel content and porosity integrity was necessary to maximize the catalytic activity. The high porosity is particularly relevant in the heterogeneous catalytic transformation of PMS because it provides a larger surface area and more

active centers, thus becoming more reactive.

The chemical composition and oxidation state of the NiPt films is also especially relevant to efficiently activate the PMS. It is very important to have an oxidized Ni surface, as it is known that Ni(O) frequently generates a competing reaction with PMS in which no sulfate or hydroxyl radicals are formed, thereby forcing the increase in the PMS concentration [39]. To analyze the composition of the deposited films, XPS analysis of Ni 2p and Pt 4f was performed, and the obtained binding energies were calibrated using the C 1 s peak (284.60 eV). As shown in Fig. S2, for the three deposition voltages, the Ni 2p spectra revealed that Ni(II) oxides were the most abundant superficial species. This is especially important because Ni²⁺, among other transition metal ions (e.g., Co²⁺, Mn²⁺, Fe²⁺, and Ru³⁺), has proven to be an exceptional activator of PMS [40–43]. The relative amount of metallic nickel was more relevant at less negative potentials, because the pH variation at the electrode's interface, enhanced by the presence of Pt, caused the chemical precipitation of nickel hydroxides. The contribution of metallic nickel also increased after Ar ion sputtering, thus demonstrating the formation of a highly oxidized Ni surface. At the same time, the Pt 4f spectra of the surfaces revealed the predominant presence of metallic Pt at 71.4 eV and Pt(I) at 72.3 eV, possibly due to the formation of some Pt hydroxide.

To determine and optimize the catalytic activity towards PMS activation of the mesoporous NiPt layers deposited at different voltages, their efficiency to degrade and mineralize the antibiotic tetracycline as model. Tetracycline was selected because it is an emerging pollutant with a global presence, particularly in developing countries, where large intensive livestock farms have been introduced since the late 1990 s. These farms use tetracycline as an antibiotic and growth promoter. Tetracycline presents significant persistence, and it has adverse effects on aquatic ecosystems and human health. Moreover, tetracycline analysis does not require complex techniques, being therefore an ideal model for environmental remediation assays.

The PMS activation by the mesoporous NiPt layers was analyzed under dark conditions (see Table S2). As can be observed in Fig. S3, the catalytic efficiency of the mesoporous pure Pt film was very low, showing poor tetracycline degradation and negligible mineralization. The degradation/mineralization efficiencies clearly improved when de Ni/Pt ratio increased, i.e., for higher deposition potentials. Degradation rates exceeding 90 % were observed when the Ni-to-Pt ratio was 19 after 10 min reaction. Therefore, Pt did not facilitate the catalytic process, but it was nevertheless necessary to attain the mesoporous architecture. Therefore, although Pt did not directly affect the activation of PMS, the maximization of the surface area was pivotal to increase catalytic efficiency. The mineralization values were slightly lower, as can be expected, but the same tendency was observed as a function of the Ni/Pt ratio. As a result, the optimal deposition of the mesoporous NiPt films at –1000 mV was fixed for all the subsequent experiments under illumination conditions.

We also assessed the tetracycline degradation efficiency in the presence of PMS by the nanostructured Si/Au interface with and without illumination, showing a negligible effect, as expected from the low activity of both materials to activate the PMS.

3.2. Degradation and mineralization amplification by the wireless nPEC cell

We now show the capacity to drastically accelerate the activation of the PMS with the light illumination in the monolithic nPEC cell under wireless actuation, i.e., without applying any bias voltage. We first analyzed the effect of the light intensity on the degradation efficiency during continuous wave illumination, and then the ability to amplify even further the degradation rate under pulsed actuation, thus reducing the average NIR light intensity (and the input energy) by half. The nPEC cell was totally immersed in the polluted aqueous media for all the experiments. The experiments were conducted during a short contact time of 3 min to clearly capture the amplification of the tetracycline

degradation kinetics (Fig. 2). The first interesting observations were that, even at low light intensities (e.g., 4 mW·cm^{–2}), there was a clear amplification of both the degradation and mineralization values (Fig. 2a), and this amplification steadily increased with the light intensity. After only 3 min of reaction, a degradation exceeding 65 % and nearly 30 % mineralization were achieved when the nPEC cell was irradiated with a light intensity of 20.6 mW cm^{–2}, which corresponds to a remarkable 8.6-fold and 14.1-fold amplifications of the degradation and mineralization efficiencies, respectively, with respect to the dark condition. It is worth highlighting that such light intensity is ca. 5-fold lower than sunlight.

As the degradation rate peaked at a light intensity of 20.6 mW cm^{–2}, this intensity was chosen for subsequent experiments. However, it is possible that even higher degradation efficiencies could be achieved at higher intensities, which could not be attained with our setup.

The effect of the pulsed light on the tetracycline degradation and mineralization efficiencies was even more striking. Although the amount of incident photons was twice lower, the pulsed light was able to amplify even further both degradation and mineralization of tetracycline. In these cases, the degradation of the antibiotic was practically completed with the pulsed light at 100 Hz and 500 Hz frequencies after only 3 min of reaction (see Fig. 2b and Table S4), and achieved outstanding values of mineralization of 39.5 % and 59.2 %, i.e., 18-fold and 28-fold amplification, respectively, compared to the dark condition. Importantly, complete mineralization could be fully achieved by just increasing the reaction time up to 10 min, as can be observed in Fig. S3–4, for the illumination at 20.6 mW·cm^{–2} and 500 Hz modulation. Again, it should be emphasized that these results were obtained with an average light intensity that was ca. 10-fold lower than the sunlight, and with safe low energy NIR light. Moreover, we used small nPEC cells with light and catalytic active cross-sections of only 1 cm² and 0.5 cm², respectively, without applying any bias voltage.

The nPEC system exhibited notably superior performance for the degradation and mineralization of tetracycline compared to various other strategies employing catalytically activated PMS with heterogeneous systems [44–51] (see Table S5), particularly considering the low amount of catalyst (between 45 µg mL^{–1} and 55 µg mL^{–1}). For example, Cu-doped CoOOH achieved tetracycline degradation rates as high as 97.7 % in 10 min, yet their mineralization rates reached only 51.5 % [44]. In other examples, around 90 % degradation could be obtained in 40 min for single-atom Fe-g-C₃N₄ catalysts [45], ca. 98 % in 60 min for WO₃/BiOBr [46], roughly 80 % in 40 min with CoO@Co-N-GC [47], about 94 % in 60 min in Ag/MoS₂@Fe-CS catalysts [48], 98 % in 12 min in Ca-Co bimetallic catalyst [50], and a remarkable degradation of 99.6 % in 24 min, but with mineralization rates below 56 % with Co–Zn–N–C catalysts [51]. In the case of SrTiO₃/BaFe₁₂O₁₉ catalysts stimulated with visible light, approximately 96 % degradation was obtained in just 1 min, but the mineralization rates were less than 40 % [49], even at much longer reaction times, and the quantity of employed catalyst was ca. 20-fold higher. Hence, none of the previously mentioned PMS catalysts approached the mineralization rates achieved by the proposed nPEC system, underscoring its remarkable competitiveness, especially considering the low quantity of catalyst per nPEC cell. As additional advantage, the NiPt catalyst is supported on the nPEC cells, thereby avoiding the need of any filtration steps to remove and recover the catalyst.

To investigate the role of reactive species formed by the PMS activation process, free radical quenching experiments using EtOH and TBA as scavengers were performed (Fig. 2c). In general, hydroxyl and sulfate radicals are quenched by EtOH, whereas hydroxyl radicals are quenched by TBA. The reaction constant between hydroxyl radicals and TBA (3.8·10⁸–7.6·0⁸ M^{–1} s^{–1}) is significantly larger than that between TBA and sulfate radicals (4.0·10⁵–9.1·10⁵ M^{–1} s^{–1}), while the kinetic constant between hydroxyl and TBA and sulfate and TBA are quite similar [52–54]. A comparison of the degradation values in the presence of these quenching agents clearly distinguishes the effects of both radical species. Fig. 2c demonstrates that the formation of sulfate radicals was

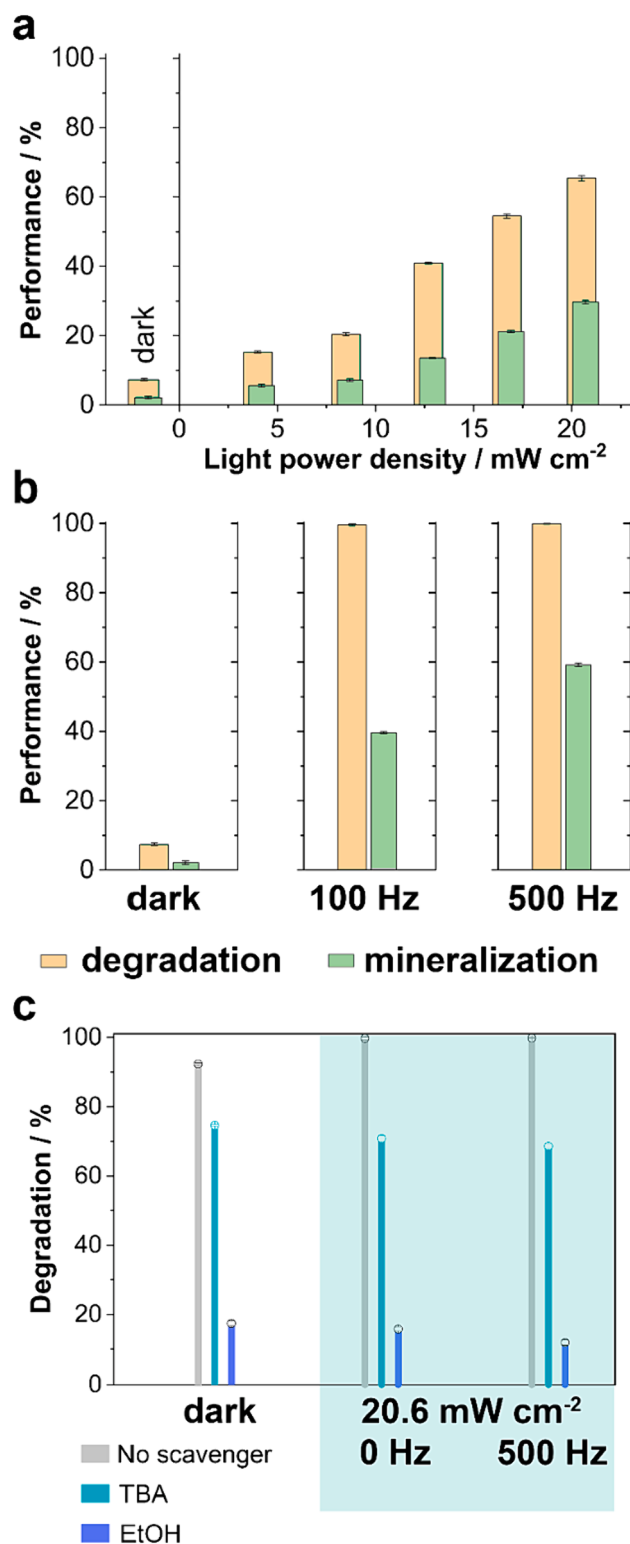


Fig. 2. Demonstration of the amplification of tetracycline degradation and mineralization by the nPEC cell illuminated with continuous and pulsed light. a) Tetracycline degradation and mineralization after 3 min of treatment as a function of the continuous wave light intensity. b) Tetracycline degradation and mineralization of nPEC cell, after 3 min, in dark and under pulsed (frequencies 100 Hz and 500 Hz) light irradiation (20.6 mW cm^{-2}). The error bars indicate the standard deviations from three replicate experiments. c) Effect of *tert*-butyl alcohol (TBA) and ethanol (EtOH) as radical quenchers in the degradation of tetracycline after 10 min in the dark and under continuous and pulsed light irradiation (highlighted area). Experimental conditions: 20 ppm of tetracycline, [PMS] = 0.3 mM, T = 20 °C, and pH 7.0.

the primary driver of degradation, irrespective of irradiation conditions. The capture of sulfate and hydroxyl radicals led a drastic decrease of the tetracycline degradation rates, dropping from approximately 92 % and 100 % to approximately 12 % and 17 %. In contrast, when the hydroxyl quencher was used, degradation rates between 69 % and 74 % were obtained. Thus, although the formation of hydroxyl radicals has a non-negligible effect on the degradation, sulfate radicals play the predominant role.

To comprehensively understand the role of the sulfate and hydroxyl radicals on the mineralization process, quantitative measurements were conducted using spectrophotometric methods (Fig. 3). Fig. 3b-c illustrate that the concentration of Ce(IV), which directly correlates with the quantity of the generated sulfate radicals, was approximately 5.1 and 3.4-fold higher under pulsed light and continuous light conditions, respectively, compared the nPEC cell in darkness. In the absence of light, the NiPt catalyst exhibited a noteworthy rate of sulfate radical formation, but the continuous and pulsed illumination induced a remarkable amplification.

As PMS can also react with metallic Ni without generating radicals, it is necessary to determine whether the nPEC cell favors the sulfate radical formation. Fig. 3e illustrates the temporal evolution of PMS concentration. The PMS degradation followed a similar trend as the sulfate radical formation, showing amplified decomposition when the nPEC cell was irradiated with continuous light and, even more, with pulsed light. Considering the rates of radical formation and PMS decomposition, it can be inferred that light actuation significantly amplified radical formation. It is worth highlighting that the pulsed irradiation enabled nearly 90 % conversion of the initial PMS into sulfate radicals.

The amount of generated hydroxyl radicals was also quantified in the dark and under continuous or pulsed light irradiation. It is important to note that sulfate radicals can quickly convert to hydroxyl radicals by reacting with water molecules, especially under slightly alkaline conditions. In the absence of PMS and illumination, no hydroxyl radicals were formed. In contrast, in the presence of PMS and under the influence of both continuous and pulsed light, the rate of hydroxyl radical formation increased up to 7.6 and 10.4-fold, respectively, compared to the rate obtained in the dark. Nevertheless, considering that fluorescein was in the micromolar range, the quantity of hydroxyl radicals generated during the irradiation process was significantly lower than that of sulfate radicals.

3.3. Understanding the degradation amplification by the wireless nPEC cell

We hypothesize that the strong amplification efficacy of the nPEC cells is due to two main opto-electric effects. The first is the efficient accumulation of the photogenerated holes in the mesoporous Ni-rich NiPt network, which enables maintaining the adequate oxidized state of the Ni surface. The second effect is the photovoltaic induced increase in the PMS mass transport in the mesoporous structure. The illuminated nPEC cell acts as a capacitor in which the photogenerated holes are concentrated in the mesoporous NiPt layer (Fig. 1a), thereby generating a positive surface potential. This potential electrostatically attracts the negatively charged PMS molecules to the catalytic surface and, therefore, drastically increases the PMS activation rate to generate the radical species. However, when the light illumination is constant, the formation of the dielectric double layer and the accumulation of negatively charge species inside the mesoporous NiPt matrix can hamper the adequate access of new PMS molecules to the active surface, as well as the exit of the negatively charged sulfate radicals. This adverse effect can be minimized by using the pulsed light beam. In this case, a dynamic double layer is formed at the NiPt surface, which enables simultaneously enhancing the access of the PMS molecules to the catalytic surface, and the efficient release of the generated negatively charged sulfate radicals, thus maximizing the tetracycline degradation efficiency. This effect is

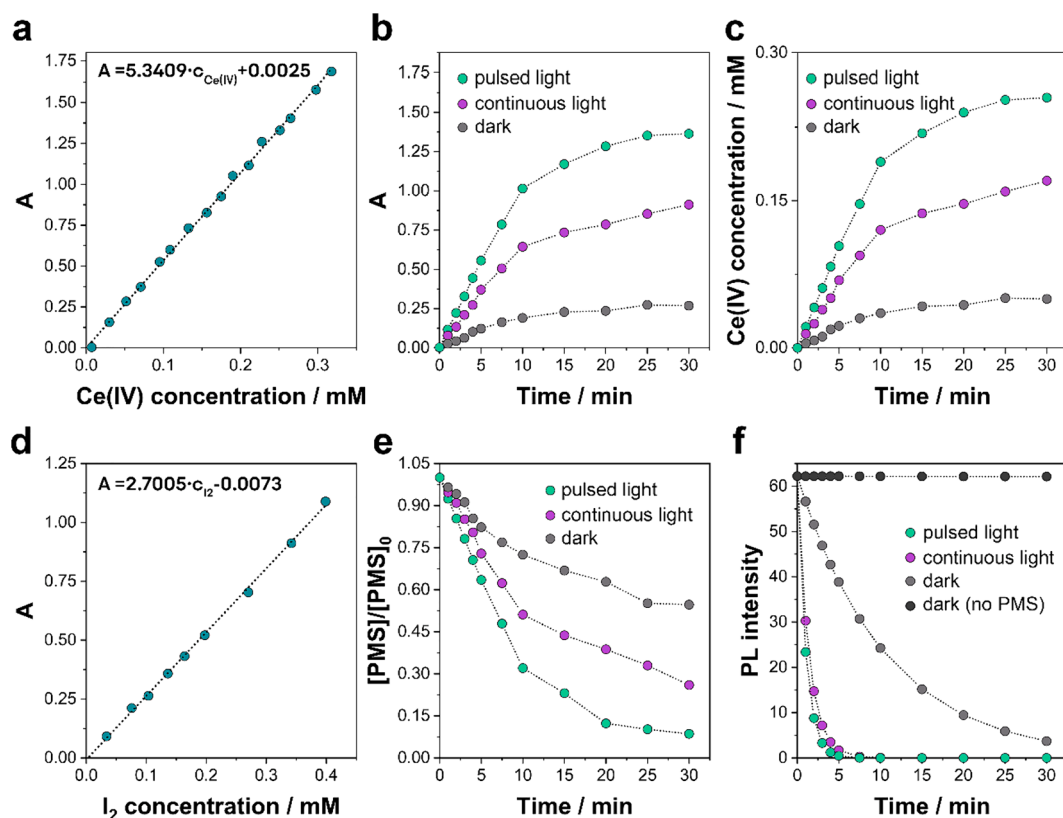
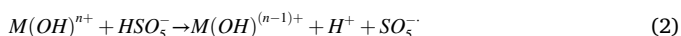
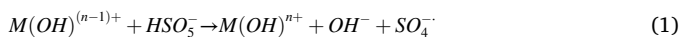


Fig. 3. Determination of the concentration of sulfate and hydroxyl radicals. a) Calibration curve for Ce(IV) ion determination via UV-vis absorbance (A) spectrophotometry (cell length = 1.0 cm, $T = 20\text{ }^{\circ}\text{C}$, pH 7.0). b) Time-dependent UV-vis absorption of Ce(IV) ions and c) concentration of Ce(IV) ions formed during nPEC cell operation under dark, continuous, and pulsed (500 Hz) light irradiation (20.6 mW cm^{-2}). Experimental conditions: [PMS] = 0.3 mM, $T = 20\text{ }^{\circ}\text{C}$, pH 7.0. d) Calibration curve for triiodide ion determination via UV-vis spectrophotometry (cell length = 0.1 cm, $T = 20\text{ }^{\circ}\text{C}$, pH 7.0). e) Time-dependent evolution of PMS concentration during nPEC cell operation under dark, continuous, and pulsed (500 Hz) light irradiation (20.6 mW cm^{-2}). Experimental conditions: [PMS] = 0.3 mM, $T = 20\text{ }^{\circ}\text{C}$, pH 7.0. f) Time-dependent photoluminescence (PL) spectra of $8\text{ }\mu\text{M}$ aqueous solution during nPEC cell operation under dark, continuous, and pulsed (500 Hz) light irradiation (20.6 mW cm^{-2}). Experimental conditions: [PMS] = 0.3 mM, $T = 20\text{ }^{\circ}\text{C}$, pH 7.0.

supported by the additional improvement of the degradation and mineralization efficiencies when the pulse frequency increases, thereby maximizing the dynamic mass transport rate of reactants and products. This effect is probably also aided by the average higher photovoltage at 500 Hz (Fig. 1e), as a consequence of the slow capacitive discharge at this frequency.

To demonstrate the first hypothesis, we analyzed the catalytic efficiency and the oxidation state of the NiPt films after 30 consecutive cycles of 10 min reaction in the dark and under constant light irradiation conditions (Fig. 4a). In the absence of light, the degradation and mineralization rates showed a clear and monotonic drop after the seventh cycle. By contrast, under light irradiation, the degradation efficiency maintained relatively similar values across the 30 cycles, whereas the mineralization only showed a slight decrease after 12 runs. The PMS activation and formation of sulfate radicals normally exhibit the following mechanism when transition metals are used as activators [39,55]:



Therefore, the electron-hole pair formed during irradiation not only enhanced the degradation and mineralization kinetics, but also significantly improved the reusability of the catalyst by maintaining a robust oxidized Ni surface. To confirm it, the chemical nature of the NiPt film after the 30 cycles in the dark and under light irradiation was further investigated by XPS. In dark conditions, the Ni 2p spectra

(Fig. 4b) revealed that Ni(II) was the dominant species, whereas the amount of Ni(III) was significantly lower, as evidenced by the intensity of the binding energies at 855.5 eV (Ni 2p_{3/2}) and 873.0 eV (Ni 2p_{1/2}) for Ni²⁺ and 856.7 eV (Ni 2p_{3/2}) and 874.2 eV (Ni 2p_{1/2}) for Ni³⁺. In contrast, under irradiation, the amount of Ni(III) was significantly higher than in the dark. It should be noted that in the mechanism proposed above, Ni(II) is oxidized upon reacting with PMS, which results in the formation of sulfate radicals. Moreover, Ni(III) is also reduced to Ni(II) upon reacting with PMS, thus generating peroxymonosulfate anion radicals ($^{\cdot}O_3SOO^-$ or $SO_5^{\cdot-}$). Therefore, the photogenerated holes favor the oxidation of Ni(II) to Ni(III) and thereby enhance the PMS activation.

In addition, the electrostatic interactions at the catalytic interface caused by the photovoltaic actuation on both reactants and products can also be crucial to amplify the pollutant degradation efficiency. As discussed above, the NiPt layer is positively charged under irradiation conditions due to the accumulation of holes in this layer. Therefore, to confirm the relevance of the electrostatic interactions we exploited the capacity to tune PMS charge with the pH. At low pH, PMS predominantly exists in its protonated neutral form, whereas PMS is negatively charged at higher pH. Several studies have reported that the optimal pH range for PMS activation lies between 7 and 9, in which PMS undergoes partial dissociation, leading to the efficient production of sulfate radicals. However, at even higher pH values, the competition between PMS dissociation and sulfate radical scavenging reactions can reduce the sulfate radical yield. Taking this into consideration, we compared the tetracycline degradation and mineralization at pH 4.5, 7.0 and 8.0 when the nPEC cell was illuminated by the 500 Hz pulsed light with a peak intensity of 20.6 mW cm^{-2} . At pH 4.5 (i.e., neutral PMS), the

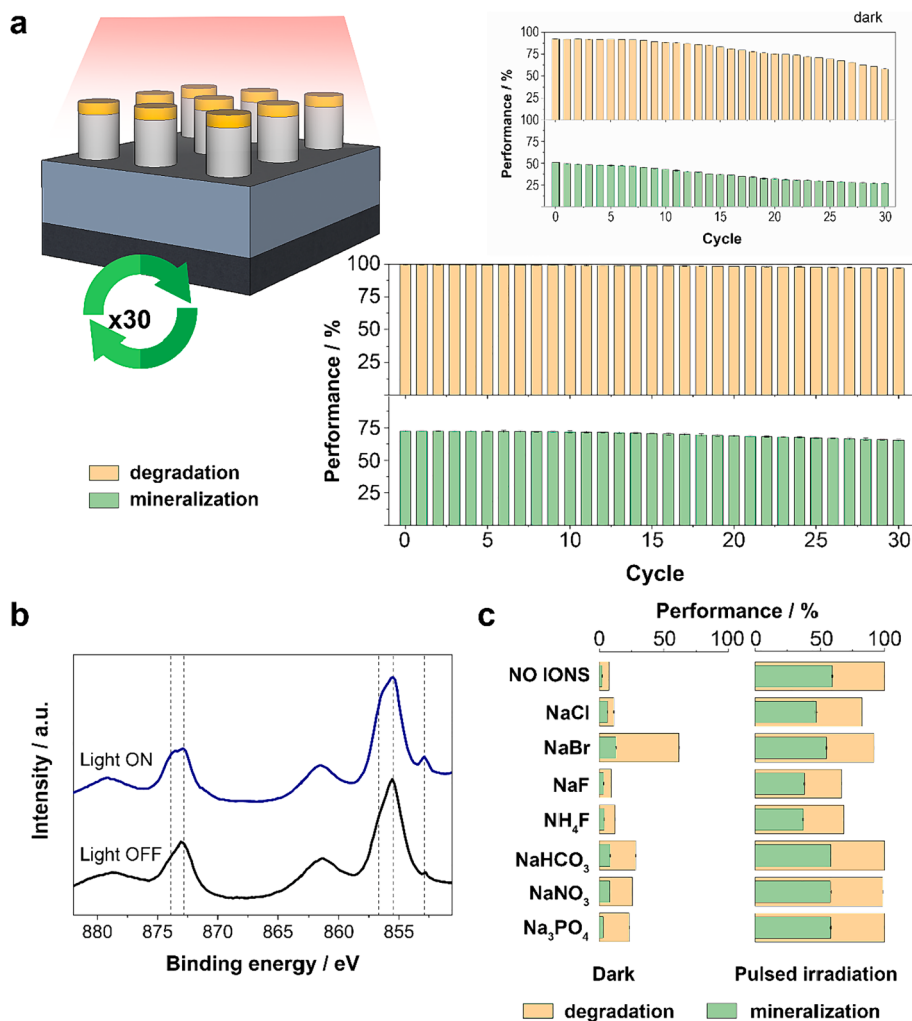


Fig. 4. Analysis of the photo-electrochemical effects. a) Reusability of the nPEC cells during 30 consecutive 10-min reaction cycles for the degradation and mineralization of tetracycline in the dark and under irradiation with a constant light intensity of 20.6 mW cm^{-2} . Experimental conditions: 20 ppm of tetracycline, $[\text{PMS}]_0 = 0.3 \text{ mM}$, $T = 20^\circ \text{C}$, and $\text{pH } 7.0$. b) XPS spectra of Ni 2p for Si(n)-Au/Si(p)@NiPt after 30 degradation cycles in the dark or under light irradiation. c) Influence of different ions on the PMS-catalyzed degradation and mineralization in the dark and under pulsed light irradiation (20.6 mW cm^{-2} and 500 Hz). Salt concentration: 10 mM. Experimental conditions: 20 ppm of tetracycline, $[\text{PMS}]_0 = 0.3 \text{ mM}$, $T = 20^\circ \text{C}$, and $\text{pH } 7.0$.

degradation and mineralization rates showed a drastic decrease by approximately 70 % and 86 %, respectively, compared to the values obtained at $\text{pH } 7.0$. On the other hand, at $\text{pH } 8.0$, the degradation efficiency was only marginally lower than at $\text{pH } 7.0$, with a reduction of approximately 11 % and 15 % in the degradation and mineralization, respectively. These results confirm that electrostatic interactions play a crucial role to amplify the catalytic performance of the system.

In contrast, the electrostatic interactions between the pollutant and the nPEC are not so relevant, since tetracycline degradation is carried out by the released sulfate and hydroxyl radicals in solution, as confirmed by the radicals quenching experiments (Fig. 2e). Actually, at $\text{pH } 7.0$, tetracycline exists primarily in its zwitterionic form, with more than 80 % of molecules exhibiting no net charge and, consequently, showing null electrostatic interaction with the positively charged NiPt interface. However, a non-negligible percentage of molecules has a negative charge, leading to favorable electrostatic interactions under irradiation between the surface and the tetracycline molecules, which could also contribute to amplify the degradation.

Considering the relevance of the electrostatic interactions between PMS and the charged interfaces of the nPEC cell, it is important to determine the potential cross talk with other inorganic ions that can be present in complex natural waters, including chlorides, nitrates, carbonates, sulfates, ammonium, and sodium. This motivated the analysis

of the impact of these ions on the degradation processes due to their potential strong influence on both radical and non-radical degradation mechanisms [56]. Six different anions (chloride, bromide, fluoride, bicarbonate, nitrate, and phosphate) and two cations (sodium and ammonium) were analyzed under pulsed light irradiation and in the dark. Bicarbonate, carbonate, and phosphate significantly increased the pH of the medium, while chloride, bromide, fluoride, and nitrate did not induce significant pH changes. The alkaline pH promotes the self-decomposition of PMS, but the sulfate and hydroxyl radicals generated can be rapidly consumed by the inorganic anions. Interestingly, after 3 min of reaction in the dark, the tetracycline degradation improved for all the ionic species, showing an enhancement of 1.5-fold for chloride, 8.3-fold for bromide, 1.2-fold for fluoride + sodium, 1.6-fold for fluoride + ammonium, 3.8-fold for bicarbonate, 3.5-fold for nitrate, and 3.1-fold for phosphate. However, the effect significantly differed depending on the type of ion, with the most relevant ones being bromide, bicarbonate, nitrate, and phosphate. Bicarbonate and phosphate anions can activate PMS, forming singlet oxygen through the nucleophilic attack of PMS, which is transformed into peroxyanions that have moderate oxidative capacity [56–58]. On the other hand, chloride and fluoride ions have a much lower impact on the degradation rate. Chloride ions undergo a two-electron reaction with PMS, forming HOCl and binary mixtures (PMS/Cl^-) with the oxidative capacity of electron-rich organic

compounds [56,59]. Recent studies have shown that bicarbonate, nitrate, and phosphate have a significant effect during the initial steps of the reaction, mainly affecting the degradation, while the impact of chloride was less relevant at the beginning, but it became more important at longer reaction times (Fig. 4c) [56]. Regarding the mineralization, all ions also contributed to improve the mineralization rate, with approximately 3.0-fold increase for chloride, 6.1-fold for bromide, 1.5-fold for fluoride + sodium, 1.8-fold for fluoride + ammonium, 4.0-fold for bicarbonate, 3.9-fold for nitrate, and 1.4-fold for phosphate. At reaction times longer than 10 min, chlorides and bromides maintained higher mineralization rates, while the rest of the ions had less impact, resulting in nearly identical mineralization values.

In contrast, the impact of the inorganic ions was less significant in the case of the nPEC cells illuminated with pulsed light for 3 min (Fig. 4c), showing similar tetracycline degradation rates for the nitrate, bicarbonate, and phosphate. However, a slight decrease of the degradation rate was observed for the chloride (1–2 fold), bromide (1.1-fold), and fluoride (1.5-fold). The same trend was observed in the mineralization rates, with only fluorides, chlorides, and bromides showing some negative influence at longer times, while negligible differences were observed with respect to sodium and ammonium. The impact of anions on the degradation and mineralization (with greater negative charges resulting in a more negative effect), confirmed the importance of the photovoltaic effects between the light-induced positively charged NiPt interface and the anions competing with the negative PMS. Despite this negative influence, Fig. 4c clearly shows that the pulsed light actuation can generate a large amplification of the tetracycline degradation rate, even in the presence of large concentrations of competing negative ions.

Finally, to further clarify the working principle of the wireless nPEC cells, we examined the tetracycline degradation and mineralization after blocking either the NiPt catalytic interface or the light active Si/Au interface, by depositing a non-permeable transparent acrylic resin (see Table S2). When the mesoporous NiPt was blocked, the degradation and mineralization presented very low values. By comparison, when the Si/Au photocathode surface was blocked, the catalytic activity only slightly decreased (ca. 20 % in degradation and 10 % the mineralization). In this case, as the resin is transparent, electron-hole pairs can be still generated and the holes concentrated in the NiPt region. Therefore, the electrochemical reduction reactions that could be generated in the Si/Au region did not play a significant role in the tetracycline degradation.

These results confirm that the NiPt layer is crucial to activate the PMS, whereas the photogenerated holes play the key synergistic role to amplify the reaction rates and enhance the durability of the device.

Although the nPEC cell was designed to maximize the light absorption efficiency in the NIR, it is possible to use any light source with emission wavelength from the UV up to 1.1 μm , which is the bandgap limit of the silicon [37]. Actually, white light sources can generate similar photovoltages as those shown in Fig. 1d (see Fig. S5 in SI), thus suggesting the same capacity to enhance the PMS activation.

3.4. Amplification of the degradation and mineralization of other relevant organic pollutants: Levofloxacin and anatoxin-A

Finally, it is essential to explore whether the remarkably amplified catalytic activity of the wireless pulsed nPEC cells exhibited in the degradation and mineralization of tetracycline can be extended to other highly relevant contaminants. To prove the efficiency and versatility of the nPEC cells, we also evaluated the degradation and mineralization two highly relevant organic pollutants whose degradation with advanced oxidation processes is much more difficult than tetracycline. The first pollutant was levofloxacin, which is one of the most widely extended antibiotics worldwide. The presence of this antibiotic in waste water can contribute to develop and spread antibiotic-resistant bacteria, as well as to disrupt the natural microbial communities in aquatic ecosystems. The second pollutant was biotoxin anatoxin-A, which is a potent neurotoxin produced by cyanobacteria (blue-green algae) found

in freshwater. The contaminated wastewater with anatoxin-A can poison aquatic organisms, disrupting the food chain and cause ecological imbalances, even at very low concentrations. Therefore, the efficient elimination of both pollutants is crucial to ensure safe drinking water.

Fig. 5 illustrates the impact of treatment time of the nPEC cell in the dark and under irradiation with continuous (0 Hz) or pulsed (500 Hz) light for both organic pollutants (Tables S6 and S7). As can be observed, the PMS activation was not as efficient as in the case of tetracycline, due to the different chemical composition of the pollutants, showing lower degradation and mineralization values in the dark, even after 30 min of reaction. In contrast, a large amplification was observed again by light illumination under constant intensity and, even more pronounced, under pulsed illumination. The powerful amplification can be clearly seen in the case of levofloxacin pollutant. While the degradation and mineralization rates after 30 min reaction were below 25 % in the dark, complete degradation and nearly 50 % mineralization was achieved

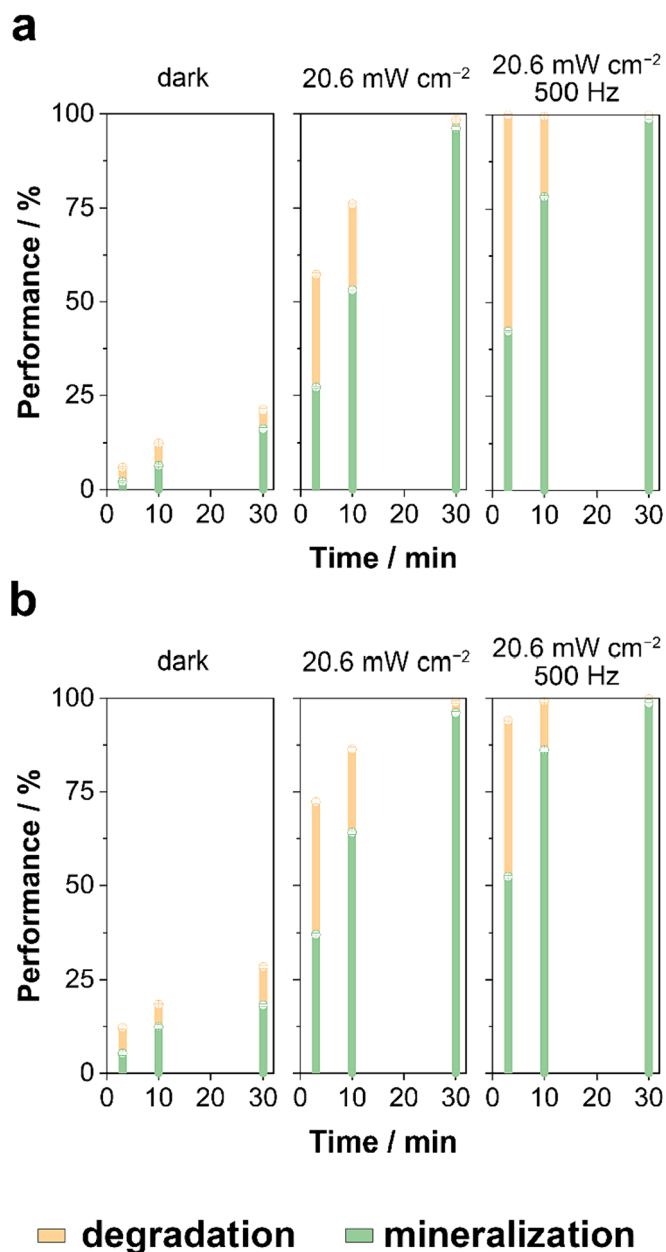


Fig. 5. Degradation and mineralization of (a) levofloxacin and (b) anatoxin-A under different conditions. Experimental conditions: 20 ppm of levofloxacin or 5 ppm of anatoxin-A, $[\text{PMS}]_0 = 0.3 \text{ mM}$, $T = 20^\circ\text{C}$, and $\text{pH } 7.0$.

with the pulsed illumination after just 3 min reaction. A similar trend was observed for the anatoxin-A. Moreover, after 30 min reaction complete mineralization of both compounds was attained by the pulsed light illumination. These results indicate that the wireless pulsed nPEC cell approach can be applied to drastically enhance the degradation rate of other highly persistent organic contaminants.

4. Conclusions

We have presented a novel concept of nanostructured photoelectrochemical cell for the highly amplified degradation of organic pollutants. The nPEC cell has been designed to monolithically integrate: (i) a photovoltaic cell with improved light absorption efficiency in the NIR, and (ii) an optimized catalytically active mesoporous NiPt layer for the activation of PMS to efficiently generate highly reactive sulfate and hydroxyl radical. This configuration has enabled wireless actuation without the need for any applied bias voltage, thus drastically simplifying and reducing the cost of the device. The nPEC cell can be driven by low intensities (ca. 10-fold lower than sunlight) of light from the UV to the NIR (up to 1.1 μm wavelength) to generate photovoltages up to 500 mV (Fig. S5), with minimal energy costs. In the three analyzed pollutants (tetracycline, levofloxacin and anatoxin-A), over one order of magnitude amplification of the degradation and mineralization rates have been demonstrated after only 3 min of reaction. Such high amplification has been achieved by the synergistic effects of the photogenerated holes, which can preserve and even increase the oxidation state of the Ni surface to efficiently activate the PMS, and the electrostatic interactions between the light induced positively charged surface of the NiPt network and the negatively charged PMS. The combination of both effects explains: (i) the even higher catalytic amplification observed with pulsed light due to the formation of a dynamic dielectric double layer that maximizes the PMS mass transport and the release of the dominant sulfate radicals, and (ii) the enhanced durability of the nPEC cells under illumination.

This technology represents an important step towards improved advanced oxidation processes with minimal energy input requirements, particularly with pulsed light, which enables a 2-fold reduction of the input energy. The interest of the technology is also reflected by the simplicity of the wireless actuation, and the scalability of both the nanopatterning process based on large scale colloidal lithography and the electrochemical deposition of the Ni-rich mesoporous NiPt layer. The nPEC cell amplifying the PMS activation constitutes a very general and powerful pathway that could be applied to degrade and mineralize nearly any organic pollutant. This concept could be extended to other photovoltaic cells providing larger photovoltages than monocrystalline silicon photodiodes, and to other transition metal oxides as catalysts to amplify the PMS activation with pulsed visible and NIR light. In these systems, to ensure the amplification of the PMS activation, a high surface area in the transition metal-oxide layer and adequate transfer of the photogenerated holes to the metal-oxide/liquid interface would be necessary. In addition, the nPEC cells could be applied to amplify the reaction rate in a wide range of chemical reactions involving charged species.

CRedit authorship contribution statement

Albert Serrà: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Elvira Gómez:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Nour al Hoda al Bast:** Methodology, Investigation. **Yue Zhang:** Methodology, Investigation, Data curation. **Marcos Duque:** Methodology, Investigation, Data curation. **María José Esplandiú:** Writing – review & editing, Visualization, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition.

Jaume Esteve: Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation. **Josep Nogués:** Writing – review & editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation. **Borja Sepúlveda:** Writing – review & editing, Writing – original draft, Validation, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data related to this article can be found, in the online version, at doi:

Appendix B. Supplementary data

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