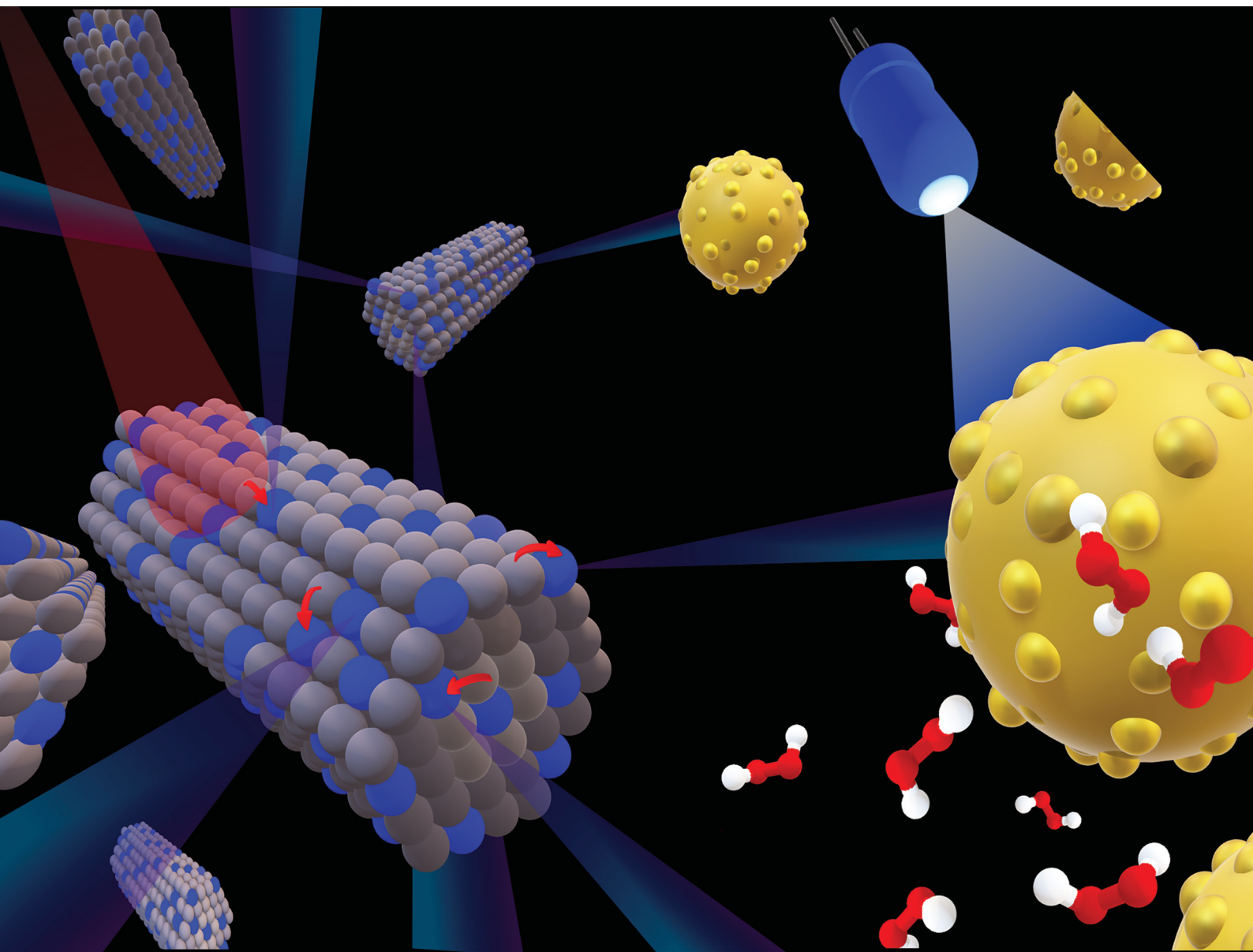


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**PAPER**

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A UV-visible-NIR active smart photocatalytic system based  
on  $\text{NaYbF}_4:\text{Tm}^{3+}$  upconverting particles and  $\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$   
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# A UV-visible-NIR active smart photocatalytic system based on NaYbF<sub>4</sub>:Tm<sup>3+</sup> upconverting particles and Ag<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> for photocatalytic processes under light on/light off conditions†

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The development of broad-spectrum photocatalytic materials that allow the use of a larger portion (UV to NIR) of the solar spectrum for photocatalytic processes has attracted great attention. Among visible light-active photocatalysts, silver phosphate (Ag<sub>3</sub>PO<sub>4</sub>) stands out prominent for its high photocatalytic activity towards the degradation of different pollutants. However, the full potential of this photocatalyst is limited by its inherent low photostability arising from self-photoreduction and its inability to efficiently use light beyond the UV-Vis range of the solar spectrum. To address these fundamental limitations of Ag<sub>3</sub>PO<sub>4</sub>, we have developed a smart photocatalytic system by combining the interesting upconversion property of NaYbF<sub>4</sub>:Tm<sup>3+</sup> upconverting particles (UCPs) with the exceptionally high photocatalytic activity of Ag<sub>3</sub>PO<sub>4</sub> and the oxidizing capacity of H<sub>2</sub>O<sub>2</sub>. In this UCPs/photocatalyst/oxidant (NaYbF<sub>4</sub>:Tm<sup>3+</sup>/Ag<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) system, the NIR-to-UV/visible UCPs can convert low energy NIR photons into high energy UV-visible photons that can be absorbed by Ag<sub>3</sub>PO<sub>4</sub>, thus photo-exciting (activating) it indirectly under NIR illumination. Similarly, the oxidant (H<sub>2</sub>O<sub>2</sub>) prevents self-reduction and/or assists in regeneration of Ag<sub>3</sub>PO<sub>4</sub> through a Fenton-like process, thus ensuring the photostability and recyclability of Ag<sub>3</sub>PO<sub>4</sub>. Interestingly, the Ag<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> system remains active generating reactive oxygen species even after the photoexcitation process is turned off (dark conditions). The proposed broad spectrum photocatalytic system (UCPs/Ag<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) was found to exhibit a high photocatalytic response (98% degradation of crystal violet dye in 90 min) under NIR illumination from a 980 nm laser and still a higher response (100% removal in less than 8 min) under direct visible light from low-cost blue emitting LEDs.

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## 1. Introduction

Considering the growing environmental problems caused by anthropogenic activities as a global concern,<sup>1–4</sup> the development of strategies and methods to counter these problems has become an active research area.<sup>5–12</sup> Among environmental remediation strategies, heterogeneous photocatalysis based on semiconductor photocatalysts has so far been the most promising strategy with greater potential for combating environmental pollution on one hand and clean energy generation on the other.<sup>13–18</sup> Unfortunately, most of the best known and commonly used semiconductor oxide photocatalysts are wide

band semiconductors (TiO<sub>2</sub> and ZnO, for example) and thus can only be photoactivated using ultraviolet (UV) radiation<sup>17,19–24</sup> which is only around 5–6% of the solar spectrum. On the other hand, relatively narrow band photocatalysts (BiVO<sub>4</sub>, CdS, ZnSe, Ag<sub>3</sub>PO<sub>4</sub> and Ag<sub>2</sub>O) exhibit photocatalytic activity under UV and visible (Vis) light,<sup>25–28</sup> but often suffer from fast electron–hole recombination and limited photostability. For example, Ag<sub>3</sub>PO<sub>4</sub> has been found to exhibit high photoactivity and thus high contaminant removal performance, but it shows low photostability and is photo(self)reduced (Ag<sup>+</sup> + e<sup>−</sup> → Ag) during the photocatalytic process by the photoexcited conduction band (CB) electrons,<sup>29–32</sup> thus limiting the recyclability of the photocatalysts.

One of the strategies to inhibit photocorrosion of Ag<sub>3</sub>PO<sub>4</sub> is to prepare its composites with other electron-acceptor materials of adequate conductivity such as graphene oxide (GO) which can remove the photoexcited electrons from the CB of Ag<sub>3</sub>PO<sub>4</sub>. For instance, Q. Xiang and co-workers prepared GO-Ag<sub>3</sub>PO<sub>4</sub> composites in which the photoactive component (Ag<sub>3</sub>PO<sub>4</sub>)

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exhibited improved photostability, a smaller particle size and reduced charge carrier recombination, thus leading to enhanced overall photocatalytic activity.<sup>33</sup> The same results can be achieved and photo(self)reduction of  $\text{Ag}_3\text{PO}_4$  can be prevented if the photocatalytic experiments are performed in an oxidizing environment, such as in the presence of  $\text{H}_2\text{O}_2$  discussed in this article.

Furthermore, the presence of GO also provides additional active adsorption sites for effective adsorption of target molecules. Since adsorption plays an important role in photocatalytic reactions, enhanced photocatalytic degradation of pollutants has been reported for GO supported  $\text{Ag}_3\text{O}_4$  and silica-supported  $\text{TiO}_2$  materials.<sup>33,34</sup> Similarly, the enhanced  $\text{CO}_2$  photoreduction capability of nanosheet-assembled  $g\text{-C}_3\text{N}_4$  has been associated with its high specific surface area and number of active sites and/or improved adsorption capacity towards  $\text{CO}_2$ .<sup>35,36</sup> Moreover, supported photocatalysts often exhibit increased active sites accessible for surface reactions. For instance, EPR studies of the mechanism of enhanced photocatalytic activity showed that the number of spins per gram (representing active sites) on the surface of silica-supported  $\text{TiO}_2$  ( $1.6 \pm 0.3 \times 10^{18}$  spin  $\text{g}^{-1}$  of  $\text{TiO}_2$ ) is higher as compared to pure or unsupported  $\text{TiO}_2$  ( $0.6 \times 10^{18}$  spins  $\text{g}^{-1}$  of  $\text{TiO}_2$ ), which partly explains the higher photoactivity of the former.<sup>34</sup>

Like any photocatalyst, the photocatalytic activity of  $\text{Ag}_3\text{PO}_4$  strongly depends on its particle size and the rate of charge carrier recombination, and decreasing these two parameters leads to improved photocatalytic activity.<sup>33</sup> Although a narrow band gap is often useful for utilization of visible light, the position of the valence band (VB) and CB plays an important role in the formation of reactive oxygen species (ROS) and consequently the redox reactions of target molecules on the surface of the photocatalyst. For instance, the VB potential of  $\text{Ag}_3\text{PO}_4$  is not positive enough to produce hydroxyl radicals ( $\text{OH}^\bullet$ ) from  $\text{H}_2\text{O}/\text{OH}^-$ , but  $\text{Ag}_3\text{PO}_4$  can produce superoxide ( $\text{O}_2^{\bullet-}$ ) radicals from the reduction of  $\text{O}_2$  present on or in the vicinity of the photocatalyst surface.<sup>33</sup>

Many attempts have been made to prepare new or modified and recyclable broad spectrum photocatalytic systems that can make use of a wider range of solar radiation (from UV to NIR), especially the NIR range which constitutes  $\sim 50\%$  of incident solar radiation.<sup>37–40</sup> One promising strategy to extend the absorption/application range of UV-visible active photocatalysts is to couple them with lanthanide-based upconverting particles (UCPs) such as  $\text{NaYbF}_4:\text{Tm}^{3+}$  and  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Tm}^{3+}$ .<sup>41–45</sup> The UCPs can successively absorb two or more relatively low energy photons (NIR photons) *via* intermediate long-lived energy states and then emit higher energy photons (in the UV-Vis region) upon relaxation through a non-linear optical process known as upconversion.<sup>41–45</sup> During this anti-Stokes ( $\lambda_{\text{emission}} < \lambda_{\text{excitation}}$ ) process, the UCPs are excited to a higher energy level through the population of intermediate energy levels and subsequently emit a higher energy photon.<sup>44–52</sup> The photons emitted by the UCPs in the UV-Vis region can be exploited to photo-excite any photocatalysts with an adequate

band gap ( $E_g$ ) that matches the energy of the emitted photon ( $E_g = h\nu$ ). Photoexcitation of the photocatalysts and interband transitions then result in the production of oxidative holes in VB and reductive electrons in the CB for the subsequent redox reaction on the photocatalyst surface responsible for the degradation of pollutants.<sup>45,53,54</sup> Despite the theoretical feasibility of the NIR active UCPs/photocatalyst system, reported literature on this topic demonstrates the limited practical success and lower contaminant removal efficiency of the system, often requiring several hours of NIR illumination.<sup>54–58</sup> The combination of different advanced oxidation processes such as photocatalysis and Fenton-like processes using  $\text{H}_2\text{O}_2$  as an oxidizing agent is a possible strategy to address the problem of low photoactivity under NIR irradiation.<sup>59–61</sup>

In this work, we report a smart photocatalytic system based on  $\text{NaYbF}_4:\text{Tm}^{3+}$  UCPs/ $\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$  that can be activated under both direct visible light illumination from low-cost blue LEDs ( $460 \pm 10$  nm) as well as NIR illumination, thanks to the NIR-to-UV/visible upconversion by the UCPs. Moreover, not only the presence of  $\text{H}_2\text{O}_2$  improves the photoactivity and photostability of  $\text{Ag}_3\text{PO}_4$  (by oxidizing back/regenerating the photo-(self)reduced Ag back to  $\text{Ag}^+$ ), but also the process of regeneration/oxidation leads to the formation of reactive oxygen species through a Fenton-like process, even when the photoexcitation process is stopped (light off condition). The strategy proposed herein may be extended to other photocatalytic systems for improving their photocatalytic activity and recyclability under a broad range of solar radiation and illumination modes.

## 2. Experimental

### 2.1. Reagents

$\text{Yb}_2\text{O}_3$  (99.99%),  $\text{Tm}_2\text{O}_3$  (99.99%), sodium fluoride (NaF) and bovine catalase enzyme ( $>10\,000$  units per mg protein) were supplied by Sigma-Aldrich (USA). Ethylenediaminetetraacetic acid disodium salt dihydrate ( $\text{EDTA}\cdot\text{Na}_2$ ) was acquired from Merck. Nitric acid ( $\text{HNO}_3$ ) and crystal violet (CV) were purchased from Qhemis (Brazil). Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 50%), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and silver acetate ( $\text{CH}_3\text{COOAg}$ , 98%) were supplied by Synth (Brazil). All chemicals were used without further purification.

### 2.2. Synthesis of the $\text{Ag}_3\text{PO}_4$ photocatalyst

The  $\text{Ag}_3\text{PO}_4$  photocatalyst was synthesized by a facile precipitation process at room temperature,<sup>62</sup> followed by thermal treatment at  $200^\circ\text{C}$ .<sup>63</sup> Briefly, 125 mL (7.5 mmol) of silver acetate solution was added dropwise under continuous stirring to a 100 mL (2.5 mmol)  $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$  solution. The resulting yellow suspension was stirred for 30 min and the  $\text{Ag}_3\text{PO}_4$  particles were then recovered by centrifugation at 7500 rpm. The precipitated particles were washed several times with deionized water, dried in a vacuum oven at  $80^\circ\text{C}$  and finally calcined at  $200^\circ\text{C}$  for 1 h.



### 2.3. Synthesis of NaYbF<sub>4</sub>:Tm<sup>3+</sup>(0.5) UCPS

The NaYbF<sub>4</sub>:Tm<sup>3+</sup>(0.5) UCPS were synthesized by a microwave-assisted hydrothermal methodology developed by our group.<sup>44,45</sup> A commercial microwave synthesizer (Discover SP model 909 150, CEM Corp.) with a 35 mL pressure vessel (CEM Part no. 909 036) covered with a special cap (CEM part no. 909 235) provided by the manufacturer was used. Briefly, Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solutions (Ln = Yb<sup>3+</sup>, Tm<sup>3+</sup>) were prepared separately from the reaction of the respective oxides with concentrated nitric acid, followed by repeated addition/evaporation of water until the pH of the solution was around 3. The resulting solutions were standardized by titrating with a standard 0.01 mol L<sup>-1</sup> EDTA solution. Then, appropriate amounts of Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solutions (total Ln<sup>3+</sup> content = 1 mmol) were added to 10 mL (2 mmol) of EDTA solution. After stirring for 30 min, 15 mL (15 mmol) of NaF was added to the above Ln<sup>3+</sup>-EDTA solution and the resulting mixture was vigorously stirred for 30 min. The obtained colloidal suspension was subjected to microwave-assisted hydrothermal treatment for 1 h at 190 °C, 250 psi and 200 W of microwave power. The NaYbF<sub>4</sub>:Tm<sup>3+</sup>(0.5) UCPS were recovered by centrifugation at 7500 rpm and then vacuum-dried after being washed once with ethanol and twice with deionized water following centrifugation-resuspension cycles. To remove EDTA from the particle surface, the UCPS were calcined at 400 °C for 90 min.

### 2.4. Photocatalytic experiments

The photocatalytic experiments were carried out under two different illumination modes, namely blue LED illumination (direct photoexcitation of Ag<sub>3</sub>PO<sub>4</sub>) and 980 nm laser irradiation (indirect photoexcitation of Ag<sub>3</sub>PO<sub>4</sub> by the unconverted UV-visible radiation from UCPS).

**2.4.1. Visible light photocatalytic activity under 460 ± 10 nm LED irradiation.** The photocatalytic activity of the synthesized Ag<sub>3</sub>PO<sub>4</sub> photocatalyst (25 mg) under blue light irradiation provided by LEDs (460 ± 10 nm) was evaluated through photodegradation of CV dye solution (7.5 mg L<sup>-1</sup>, 30 mL). The photocatalyst/CV mixture in a glass-cylindrical-reactor (10.4 cm in diameter, 5.9 cm in height) was allowed to stir in the dark for 8 min and then exposed to blue light for another 8 min. An aliquot of 1.2 mL was collected every 2 min and centrifuged to monitor changes in the electronic absorption spectrum of the supernatant part. The experiments in the presence of H<sub>2</sub>O<sub>2</sub> were carried out using the same procedure but with the addition of 110 μL or 200 μL of 1 mol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (final H<sub>2</sub>O<sub>2</sub> concentration of 3.6 or 6.6 mmol L<sup>-1</sup>) to the 30 mL CV-Ag<sub>3</sub>PO<sub>4</sub> mixture just before starting irradiation. Sample aliquots were withdrawn at regular intervals and 30–40 μL of bovine catalase solution (0.4 g L<sup>-1</sup>) was added to each aliquot withdrawn to consume any residual H<sub>2</sub>O<sub>2</sub> and interrupt the reaction. Regeneration of the Ag<sub>3</sub>PO<sub>4</sub> photocatalysts once used in the dye degradation test (in the absence of H<sub>2</sub>O<sub>2</sub> in the reaction mixture) was performed. For this purpose, 200 μL of H<sub>2</sub>O<sub>2</sub> was added to the photocatalytic mixture at the end of degradation experiments and the photocatalyst/H<sub>2</sub>O<sub>2</sub> mixture

was kept under stirring for several hours. Finally, the regenerated photocatalyst was recovered by centrifugation and washed several times with ethanol and water.

**2.4.2. NIR photocatalytic activity evaluation.** The photocatalytic activity of the UCPS/Ag<sub>3</sub>PO<sub>4</sub> photocatalyst and UCPS/Ag<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> systems under NIR excitation (980 nm laser) was evaluated using 3 mL of CV dye solution (4 mg L<sup>-1</sup>) and 10 mg of photocatalysts (mixture of UCPS + Ag<sub>3</sub>PO<sub>4</sub> in different ratios) in a 4 mL glass vial. The CV/UCPS/Ag<sub>3</sub>PO<sub>4</sub> mixture was left in the dark overnight and then irradiated with NIR radiation using a 980 nm diode laser (DMC, Brazil) coupled to a 1.5 mm diameter optical fiber at a 2 W laser power. Sample aliquots were collected for the measurement of UV-visible absorption spectra as described in Section 2.4.1, after which the sample was transferred back to the photoreactor. Different ratios of UCPS/Ag<sub>3</sub>PO<sub>4</sub> were considered to find the optimal UCPS/photocatalyst ratio for effective dye degradation under 980 nm laser irradiation. Once the optimum ratio was found (6 mg UCPS/4 mg Ag<sub>3</sub>PO<sub>4</sub>), further experiments were carried out using this ratio in the presence of 6.6 mmol L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> to analyze its influence on the degradation of CV dye under 980 nm laser irradiation and the stability/recyclability of Ag<sub>3</sub>PO<sub>4</sub>.

### 2.5. Characterization techniques

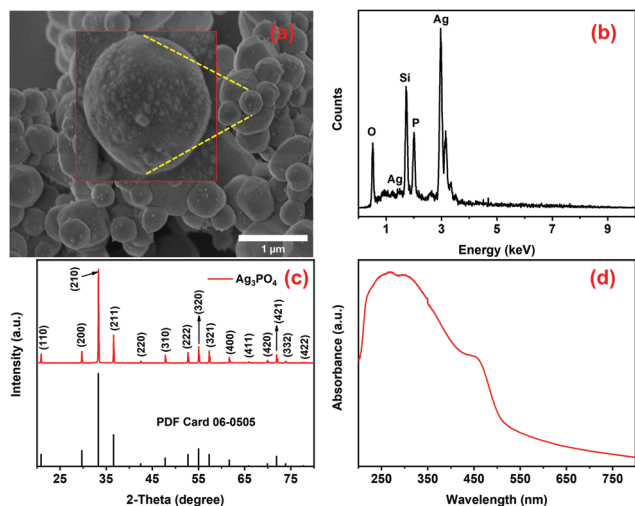
Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy measurements were performed using a field emission scanning electron microscope (FEG-SEM) (JEOL, model JSM-7500 F). Powder X-ray diffractograms (XRD) were acquired using a D8 Advance X-ray diffractometer (Bruker) operating at 40 mA and 40 kV and employing Ni-filtered Cu Kα X-ray radiation (λ = 1.540 Å). Fourier transform infrared (FTIR) spectra were obtained using a PerkinElmer Spectrum 1000 FTIR spectrometer with a resolution of 2 cm<sup>-1</sup> and averaged over four scans. Raman spectra were measured in the 100–1000 cm<sup>-1</sup> range with an acquisition time of 50 s and 2 cycles using a LabRAM HR 800 Raman spectrophotometer (Horiba Jobin Yvon) equipped with a CCD detector (model DU420A-OE-325) and a He-Ne laser (632.81 nm). The diffuse reflectance spectra (DRS) of the powder samples against a background of MgO were obtained using a Cary 5000 UV-Vis-NIR spectrophotometer (Varian). The upconversion luminescence (UCL) spectra of UCPS (8 mg of NaYbF<sub>4</sub>:Tm<sup>3+</sup>(0.5) in 10 mL of water) with an optical spectral resolution of 0.5 nm were acquired using a Horiba Jobin Yvon spectrofluorometer (Fluorolog-3 model FL3-122) equipped with a Hamamatsu R-928 photomultiplier tube. A 980 nm laser diode (DMC, Brazil) coupled with an optical fiber (1.5 mm diameter) was used as the NIR excitation source.

## 3. Results and discussion

### 3.1. Characterization of the Ag<sub>3</sub>PO<sub>4</sub> photocatalyst

The morphological, compositional, crystallographic, and optical properties of the calcined Ag<sub>3</sub>PO<sub>4</sub> particles, previously





**Fig. 1** (a) SEM image, (b) EDS spectrum, (c) XRD pattern and (d) UV-Vis-NIR absorption spectrum of the  $\text{Ag}_3\text{PO}_4$  photocatalyst. The Si signal in the EDX spectrum comes from the sample holder. The inset in a shows a magnified view of the  $\text{Ag}_3\text{PO}_4$  photocatalyst.

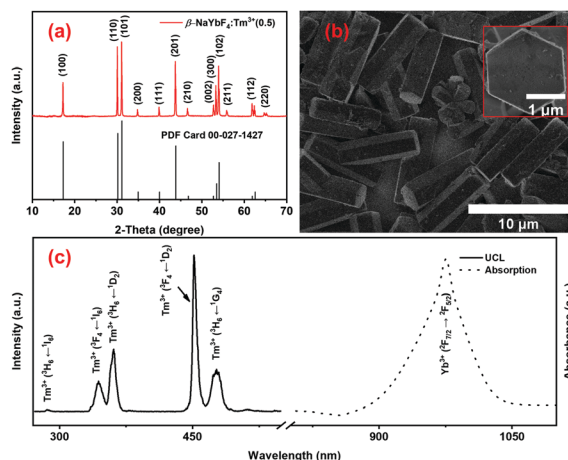
prepared by a facile room temperature method, were studied using SEM, EDX, XRD, and DRS, respectively. The  $\text{Ag}_3\text{PO}_4$  particles are micrometric (mean:  $475 \pm 182$  nm) with their surface decorated with small (approximately  $16 \pm 4$  nm size) nanospheres (Fig. 1a), as also previously observed by P. Dong and collaborators.<sup>63</sup> They reported the formation of small Ag nanoparticles, promoted by heat treatment, on the surface of calcinated  $\text{Ag}_3\text{PO}_4$ .<sup>63</sup> The EDS spectrum (Fig. 1b) shows clear emission lines of Ag, P and O, confirming the presence of these elements in the samples.

As shown in Fig. 1c, all the diffraction peaks in the diffractogram of the sample perfectly match with those of the body-centered cubic phase of  $\text{Ag}_3\text{PO}_4$  with the space group  $P43n$  (PDF no. 06-0505). The optical absorption property is an important factor that can determine the photocatalytic efficiency of materials under irradiation in a certain part of the electromagnetic spectrum and, therefore, the absorption spectrum of  $\text{Ag}_3\text{PO}_4$  powder was measured by diffuse reflectance spectroscopy (Fig. 1d). The absorption transformed DRS spectrum of the  $\text{Ag}_3\text{PO}_4$  particles shows strong absorption in the UV-Vis region (Fig. 1d), attributed to the intrinsic charge transfer of  $\text{Ag}_3\text{PO}_4$  from the VB to the CB,<sup>29,63–65</sup> with an indirect band-gap of 2.30 eV, as estimated from the Kubelka–Munk plot shown in Fig. S1a (ESI<sup>†</sup>). The strong absorption in the visible region (540–400 nm) overlaps well with the emission from blue LEDs ( $460 \pm 10$  nm), allowing effective photoexcitation of  $\text{Ag}_3\text{PO}_4$  and photodegradation of pollutants using low-cost commercial LEDs as the illumination source (*vide infra*). The  $\text{Ag}_3\text{PO}_4$  samples were also characterized by vibrational spectroscopy. The FTIR spectrum of the sample exhibits four typical FTIR bands of  $\text{Ag}_3\text{PO}_4$  (Fig. S1b, ESI<sup>†</sup>), two of which lying around  $560\text{ cm}^{-1}$  and  $1010\text{ cm}^{-1}$  are of medium/high intensity and can be attributed to the O=P–O bending vibration in the plane and the asymmetric stretching of P–O–P groups, respectively.<sup>66–68</sup> The other two bands of low intensity, situated at  $850$  and  $1385\text{ cm}^{-1}$ , are related to the

symmetric stretching vibration of P–O–P bonds and the stretching vibration of the P=O bonds in the  $\text{Ag}_3\text{PO}_4$  structure.<sup>67,69</sup> Additionally, the vibrational bands around  $3390\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$  are attributed to the stretching vibrations of O–H groups and H–O–H bending vibrations of the adsorbed water molecules, respectively.<sup>67,69</sup> Similarly, the Raman spectrum of  $\text{Ag}_3\text{PO}_4$  samples exhibits the characteristic vibrational modes of the  $\text{PO}_4^{3-}$  groups in a  $T_d$  symmetry around  $405$ ,  $550$ ,  $907$ ,  $950$  and  $1000\text{ cm}^{-1}$ ,<sup>64,70</sup> confirming the formation of  $\text{Ag}_3\text{PO}_4$  (Fig. S1c, ESI<sup>†</sup>).

### 3.2. Morphological/structural characterization and optical properties of $\text{NaYbF}_4:\text{Tm}^{3+}(0.5)$ UCPS

The structural, morphological and optical properties of the  $\text{NaYbF}_4:\text{Tm}^{3+}(0.5)$  UCPS, synthesized by a facile microwave-assisted hydrothermal method,<sup>44,45</sup> were studied using XRD, SEM and photoluminescence (PL) spectroscopy, respectively (Fig. 2). The X-ray diffraction patterns of UCPS perfectly match with the standard diffraction pattern of the hexagonal  $\beta\text{-NaYbF}_4$  phase (PDF no. 27-1427) (Fig. 2a) which is usually associated with stronger UCL than its cubic ( $\alpha\text{-NaYbF}_4$ ) counterpart. This UCP sample consists of microrods of around  $7.9 \pm 1.4\ \mu\text{m}$  length and  $2.5 \pm 0.5\ \mu\text{m}$  diameter (Fig. 2b). A magnified view of a vertically oriented microrod reveals its hexagonal shape (inset in Fig. 2b), in accordance with the results of the XRD analysis (Fig. 2a). The presence of  $\text{Yb}^{3+}$  ions and/or NIR absorption properties of the UCPS are evident from the characteristic absorption peak of  $\text{Yb}^{3+}$  at around  $975\text{ nm}$  in the electronic absorption spectrum, obtained by measuring the diffuse reflectance from the powder sample (Fig. 2c, dotted line).<sup>71</sup> The presence of  $\text{Yb}^{3+}$  thus allows the UCPS to absorb the NIR photons from a  $980\text{ nm}$  laser while doping with  $\text{Tm}^{3+}$  ions as the emitters assists in obtaining upconverted light in the UV and visible region of the spectrum (Fig. 2c, solid line). The UCL spectrum of an aqueous suspension of UCPS, measured under  $980\text{ nm}$  laser excitation, thus shows emission peaks centered around  $286$ ,  $344$ ,  $361$ ,  $452$ , and  $477\text{ nm}$  which are, respectively,



**Fig. 2** (a) XRD pattern, (b) SEM image and (c) UV-Vis-NIR absorption spectrum (dotted line) and UCL spectrum under  $980\text{ nm}$  laser irradiation (black solid line) of  $\text{NaYbF}_4:\text{Tm}^{3+}$  UCPS. The inset in b shows a magnified view of a single  $\text{NaYbF}_4:\text{Tm}^{3+}$  UCP.



attributed to the  $^1I_6 \rightarrow ^3H_6$ ,  $^1I_6 \rightarrow ^3F_4$ ,  $^1D_2 \rightarrow ^3H_6$ ,  $^1D_2 \rightarrow ^3F_4$  and  $^1G_4 \rightarrow ^3H_6$  transitions of  $Tm^{3+}$  ions (Fig. 2c, solid line),<sup>44–48</sup> as explained later.

### 3.3. Photocatalytic activity evaluation

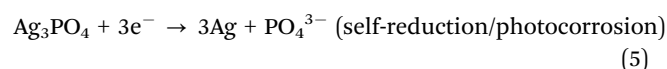
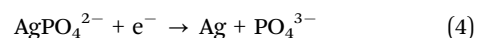
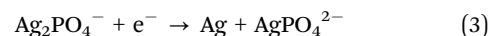
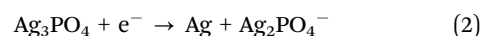
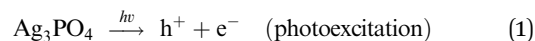
Two main objectives of the present study were to improve the photostability of  $Ag_3PO_4$  (by employing  $H_2O_2$ ) and extend the application of this photocatalyst beyond the UV-visible region and into the NIR region (by coupling UCPs with  $Ag_3PO_4$ ). Thus, detailed photocatalytic assays were performed employing  $Ag_3PO_4$  and  $Ag_3PO_4$ -UCP samples in the presence and absence of  $H_2O_2$  using either visible light from low-cost blue (460  $\pm$  10 nm) commercial LEDs or NIR light from a laser. Evolution of the photocatalytic degradation process by the  $Ag_3PO_4$ - $H_2O_2$  system under light ON/light OFF modes was also studied.

**3.3.1. Photocatalytic activity of  $Ag_3PO_4$ / $H_2O_2$  under visible light from blue LEDs.** The visible photocatalytic activity of  $Ag_3PO_4$  particles was examined under direct excitation from blue (460  $\pm$  10 nm) LEDs (Fig. 3). No significant decrease in the absorbance of CV dye was observed in the absence of  $Ag_3PO_4$ , suggesting that direct photolysis does not degrade the dye. On the other hand, in the presence of  $Ag_3PO_4$ , the normalized absorbance of the dye at around 582 nm exhibits a drastic decrease within just 2 min of LED illumination (Fig. 3a, red line) and almost 100% dye discoloration is achieved in less than 8 min (see the inset in Fig. 3a), indicating the high visible light photocatalytic activity of the prepared  $Ag_3PO_4$  particles.

Unfortunately, the high photocatalytic activity was accompanied by a change in both the morphology (Fig. S2a and b, ESI<sup>†</sup>) and color (from yellow to black) of the used photocatalyst (Fig. 3c(i)), suggesting the decomposition of the photocatalysts and/or self-reduction of  $Ag^+$  to Ag by the photoexcited CB electron.<sup>29</sup> The presence of  $H_2O_2$  in the photocatalytic reaction

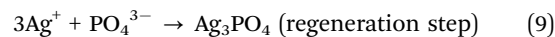
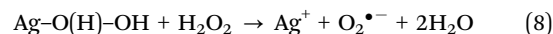
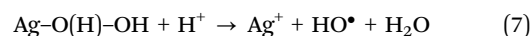
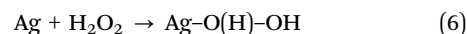
media, however, prevented any change in the morphology of the particles (Fig. S2c and d, ESI<sup>†</sup>) as well as the darkening of the photocatalyst suspension during the photocatalytic experiments (Fig. 3c(ii/iii)), without significantly affecting the original photocatalytic activity of the sample (Fig. 3b). The change in the color and morphology of the  $Ag_3PO_4$  photocatalyst during the photocatalytic experiments in the absence of  $H_2O_2$  is also accompanied by a loss in photocatalytic activity (green bar in Fig. 4), thus negatively affecting the recyclability of the photocatalyst. In fact, the observed photodegradation rate constant ( $k$ ) decreases around 10 times, going from 0.853  $min^{-1}$  (first cycle) to 0.088  $min^{-1}$  (4th cycle). The loss in photocatalytic activity in the absence of  $H_2O_2$  after repeated photodegradation cycles is attributed to the photo-assisted self-reduction of  $Ag^+$  to Ag, mediated by the photoexcited electrons in the CB of  $Ag_3PO_4$  (eqn (1)–(5)).<sup>29–32</sup>

The photo assisted self-reduction of  $Ag_3PO_4$  occurs according to the following reactions:

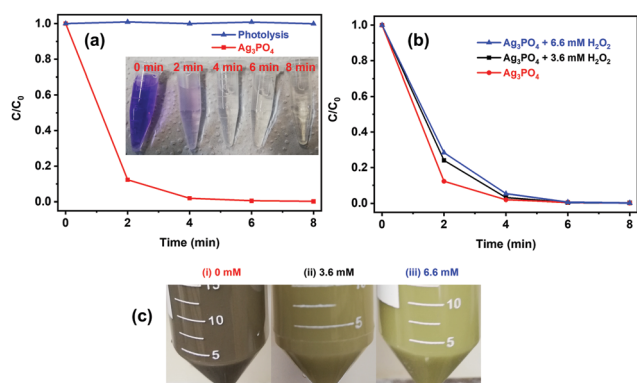


In fact, the XRD patterns of the used  $Ag_3PO_4$  show the presence of a diffraction peak of  $Ag^0$  at around 38.1° (PDF no. 65-2871) when no  $H_2O_2$  is used during the photocatalytic tests (Fig. S4, ESI<sup>†</sup>). However, the intensity of this peak is much lower when  $H_2O_2$  is added to the  $Ag_3PO_4$ /dye mixture during photocatalytic tests (Fig. S4, ESI<sup>†</sup>), indicating the importance of  $H_2O_2$  for the photostability and recyclability of  $Ag_3PO_4$ .

During the photocatalyst regeneration process,  $H_2O_2$  can oxidize the Ag back to  $Ag^+$  and thus reform  $Ag_3PO_4$  through a Fenton-like process (eqn (6)–(9)),<sup>72–76</sup> as shown below.



Control experiments in the absence of  $Ag_3PO_4$  in the reaction mixture or in the absence of LED illumination showed no significant decreases in the absorbance of the CV dye in 8 min (Fig. S3, ESI<sup>†</sup>). Although the presence of  $H_2O_2$  slightly decreased the dye degradation rate in the first photocatalytic cycle (Fig. 3b), it significantly improved the structural stability (Fig. S2 and S4, ESI<sup>†</sup>) and recyclability of  $Ag_3PO_4$  as mentioned above (Fig. 3c, 4 and Fig. S2, S4, ESI<sup>†</sup>). These results demonstrate that the presence of  $H_2O_2$  had a positive influence on the photocatalytic performance during repeated cycles of use (orange and gray bars in Fig. 4). The slight decrease in the photoactivity of the  $Ag_3PO_4$ / $H_2O_2$  system after repeated



**Fig. 3** Temporal change in the concentration of CV dye as a function of irradiation time with blue LEDs in the (a) absence (blue line) and presence (red line) of the  $Ag_3PO_4$  photocatalyst, and in the (b) absence and presence of  $H_2O_2$  in the dye- $Ag_3PO_4$  mixture. The inset in (a) shows the digital images of CV dye solution at different irradiation times (marked on the images) in the presence of the  $Ag_3PO_4$  photocatalyst. (c) Digital images of aqueous dispersions of the  $Ag_3PO_4$  photocatalyst recovered and washed after four photocatalytic cycles corresponding to the experiments carried out in the absence of  $H_2O_2$  (i) and with the addition of 3.6  $mmol L^{-1}$  (ii) and 6.6  $mmol L^{-1}$  (iii) of  $H_2O_2$ .



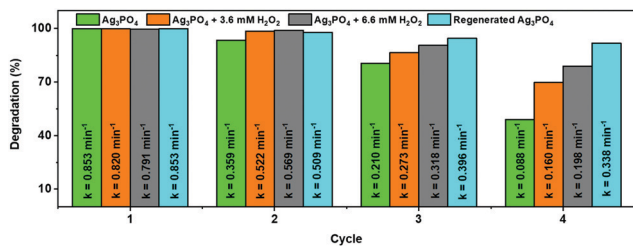


Fig. 4 Evaluation of the effect of H<sub>2</sub>O<sub>2</sub> as an auxiliary oxidizing agent on the photostability and recyclability of Ag<sub>3</sub>PO<sub>4</sub> during repeated photocatalytic degradation cycles under blue LED irradiation.

photocatalytic cycles may be related to the incomplete recovery of the photocatalyst or partial photoreduction of Ag<sub>3</sub>PO<sub>4</sub> to Ag<sup>0</sup>. Previous studies have shown that the oxygen vacancies present on the surface of Ag<sub>3</sub>PO<sub>4</sub> play an important role in its photocatalytic activity and the slight decrease in photoactivity upon repeated use may also be related to the loss of these vacancies.<sup>63</sup> Furthermore, the Ag<sub>3</sub>PO<sub>4</sub> used in the degradation experiments, without the addition of H<sub>2</sub>O<sub>2</sub>, was recovered and then regenerated with H<sub>2</sub>O<sub>2</sub> in an *ex situ* manner (Fig. S2e and f, ESI<sup>†</sup>). This regenerated photocatalyst was as efficient as the freshly prepared new photocatalysts (cyan bar in Fig. 4), thus demonstrating a remarkable recovery of its photocatalytic activity.

**3.3.2. Photocatalytic activity of the Ag<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> system after turning off the excitation light (dark).** Fig. 5 shows that, in the presence of both Ag<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>, the absorbance or concentration of CV dye continues to decrease even when the LED illumination is turned off at the end of the 4th photodegradation cycle. On the other hand, no significant post-irradiation change in concentration was observed in the absence of H<sub>2</sub>O<sub>2</sub> in the reaction mixture. Since Ag<sub>3</sub>PO<sub>4</sub> can be charged with photoinduced reductive energy by the excitation

light from LEDs (eqn (1)–(5)), this energy can then be used to produce reactive oxygen species (ROS) in the presence of H<sub>2</sub>O<sub>2</sub>, even in the dark, as can be observed from Fig. 5. The results of Fig. 5 can thus be explained based on eqn (6)–(8)<sup>72–76</sup> where the peroxide-induced oxidation of Ag<sup>0</sup> to Ag<sup>+</sup> or regeneration of Ag<sub>3</sub>PO<sub>4</sub> is accompanied by the generation of ROS (HO<sup>•</sup> and O<sub>2</sub><sup>•-</sup>) that can take part in the photodegradation of the dye even after the excitation light is turned off. Although previous studies suggest that Ag<sub>3</sub>PO<sub>4</sub> cannot produce HO<sup>•</sup> radicals from H<sub>2</sub>O/OH<sup>-</sup> as its VB edge potential is not enough, HO<sup>•</sup> radicals can be produced in the presence of H<sub>2</sub>O<sub>2</sub>, even in the dark (eqn (7)). Under adequate light illumination, Ag<sub>3</sub>PO<sub>4</sub> has been found to produce superoxide radicals (O<sub>2</sub><sup>•-</sup>) and oxidative holes that degrade the organic dye molecules.<sup>33</sup> The presence of H<sub>2</sub>O<sub>2</sub> thus not only ensures the improved photostability and recyclability of Ag<sub>3</sub>PO<sub>4</sub>, but also allows photoinduced electron storage and harnessing of the stored chemical energy for redox processes even after the photoexcitation light is turned off.

**3.3.3. Photocatalytic activity of UCPS/Ag<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> under NIR illumination.** After confirming the excellent inherent photocatalytic activity of the prepared Ag<sub>3</sub>PO<sub>4</sub> under visible light, we evaluated the NIR photoactivity of the UCPS–Ag<sub>3</sub>PO<sub>4</sub> system under 980 nm illumination from a laser (Fig. 6). A clear decrease in the absorbance of CV dyes as a function of NIR irradiation time in the presence of UCPS–Ag<sub>3</sub>PO<sub>4</sub> (Fig. 6a) and/or UCPS–Ag<sub>3</sub>PO<sub>4</sub>–H<sub>2</sub>O<sub>2</sub> (Fig. 6b) confirms the NIR-based photoactivity of the systems.

An important factor determining the degradation efficiency of a certain pollutant using the UCPS–Ag<sub>3</sub>PO<sub>4</sub> photocatalytic system is the ratio between the UCPSs and the Ag<sub>3</sub>PO<sub>4</sub> photocatalyst. A suitable UCP/Ag<sub>3</sub>PO<sub>4</sub> ratio may allow efficient absorption of the excitation (NIR) light by the UCPSs, leading to their strong UCL emission which, in turn, may efficiently

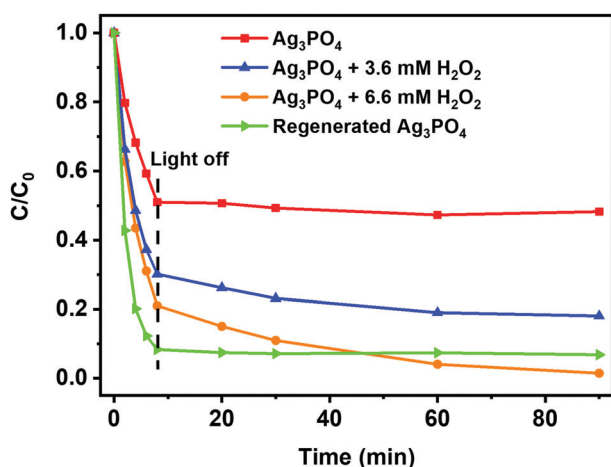


Fig. 5 Changes in the concentration of CV dye during the fourth photocatalytic cycle under irradiation (the first 8 min) and in the dark (after 8 min) using the photocatalyst recovered in the experiments performed in the absence of H<sub>2</sub>O<sub>2</sub> (red line) and in the presence of 3.6 mmol L<sup>-1</sup> (blue line) and 6.6 mmol L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> (orange line) and the regenerated material (green line).

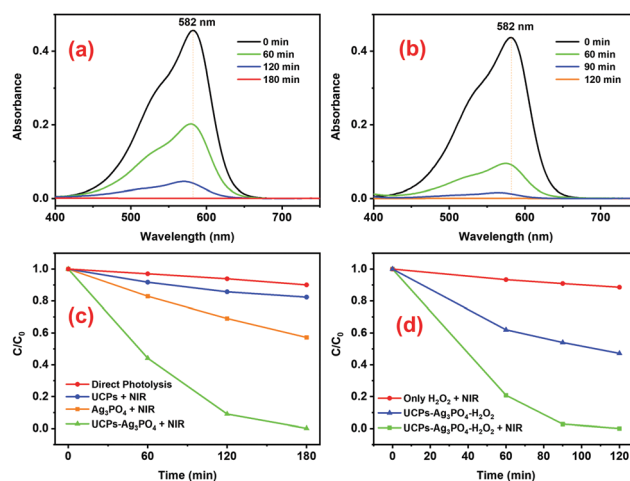


Fig. 6 Temporal evolution of the absorbance of CV under 980 nm laser irradiation in the presence of (a) UCPS–Ag<sub>3</sub>PO<sub>4</sub> and (b) UCPS–Ag<sub>3</sub>PO<sub>4</sub>–H<sub>2</sub>O<sub>2</sub> systems. Concentration profiles showing a decrease in the concentration of CV dye as a function of NIR irradiation time in the presence of (c) UCPS–Ag<sub>3</sub>PO<sub>4</sub> and (d) UCPS–Ag<sub>3</sub>PO<sub>4</sub>–H<sub>2</sub>O<sub>2</sub> systems. Different controls are also shown in (c and d).





processes after the excitation light is turned off (light off mode). Highly photoactive  $\text{Ag}_3\text{PO}_4$  particles were prepared by a simple precipitation method at room temperature. The UCPs were prepared by a facile MW-assisted hydrothermal method which allowed their crystallization in the hexagonal  $\beta$ -phase with a high NIR-to-UV/vis upconversion luminescence intensity under 980 nm laser irradiation. The upconverted UV-vis light obtained from UCPs under NIR excitation was successfully used to photoactivate the  $\text{Ag}_3\text{PO}_4$  photocatalyst, achieving a high degradation rate of crystal violet dye. It was demonstrated that the presence of  $\text{H}_2\text{O}_2$  has a positive influence on the stability of  $\text{Ag}_3\text{PO}_4$ , preventing its photocorrosion and regenerating the used photocatalysts. Importantly, the photocatalyst regeneration process also simultaneously produces reactive oxygen species in a Fenton-like manner which help in the degradation of the pollutants even when the excitation light is turned off. Moreover, the presence of  $\text{H}_2\text{O}_2$  also increased the degradation rate of the crystal violet (CV) dye under NIR irradiation, reaching an almost complete degradation of the dye in 90 min. These results indicate that the coupling between the upconverting particles and suitable photocatalysts, in combination with other advanced oxidation processes, may allow the application of photocatalytic processes in an extended region of the electromagnetic spectrum.

## Author contributions

Y. E. Serge Correales: conceptualization, methodology, investigation, visualization, writing – original draft, writing – review & editing. S. Ullah: conceptualization, methodology, visualization, writing – review & editing, supervision. E. P. Ferreira-Neto: methodology, writing – review & editing. H. D. Rojas-Mantilla: design and construction of the blue emitting LED reactor. C. Hazra: conceptualization, methodology. S. J. Lima Ribeiro: writing – review & editing, supervision, acquisition of funds, project management.

## Conflicts of interest

There are no conflicts to declare.

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