ELECTRONIC SUPPLEMENTARY INFORMATION

Feroxyhyte nanoflakes coupled to up-converting carbon nanodots: a highly active, magnetically recoverable, Fenton-like photocatalyst in the visible-NIR range

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Experimental Section

Chemicals

Potassium nitrate (≥99% KNO_3, Fluka,), Ferrous sulfate heptahydrate (≥99%, $FeSO_4{\cdot}7\,H_2O$, Aldrich), Sodium hydroxide (≥98% NaOH, Aldrich), L-lysine crystallized (≥98% $C_6H_{14}N_2O_2$, Aldrich), Sulfuric acid (95-98%, H_2SO_4, Aldrich), Methyl Orange (ACS reagent, 85% dye, Aldrich), Methanol (HPLC >99.9%, Aldrich), Hydrogen peroxide solution (30 wt% in H_2O, Aldrich), Terephthalic acid (98%, Aldrich).

Synthesis of δ-FeOOH nanoflakes

In a typical synthesis, two solutions, namely A and B, were prepared in deionized water and bubbled in Ar for 15 minutes to promote deoxygenation. The solution A consists of 180 mM KNO_3, 162 mM NaOH and 1.85 mM L-lysine. On the other hand, solution B was composed of 13 mM ferrous sulfate heptahydrate and 3,38 mM sulfuric acid. After de-oxygenation, each solution was placed in 60 mL plastic Becton Dickinson syringes. Solutions A and B were injected at a proper flow rate to obtain a 1 minute residence time according to the microfluidic system volume. Solution A and B streams were mixed in a PEEK polymer Y-junction under a constant flow ratio of 1:1 in order to ease the synthesis procedure. The microfluidic system is composed of two PTFE coils (1/16 inch OD and 0.04 inch ID), which are conceived as mixing and reaction stages, respectively (see Figure S1). The mixing of A and B streams was promoted by sonication in an ultrasonic bath, maintaining the bath temperature in the range of 25-30 ºC using a cooling bath. A pure oxygen gas stream was injected after the mixing coil to obtain a stable gas-liquid segmented flow in the reaction stage. The temperature at the reaction stage was set at 100 ºC maintaining the reactor pressure at 1.4 bar. The synthesized nanoparticles were centrifuged at 10,000 rpm for 10 minutes and re-suspended in distilled water.

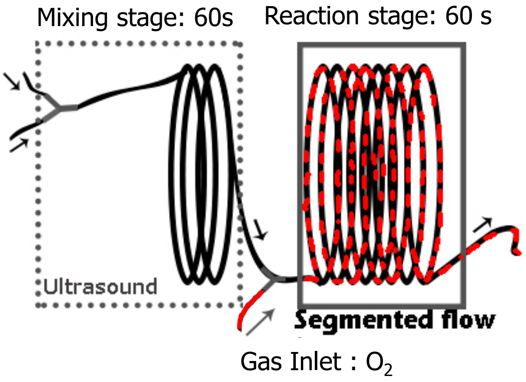


Figure S1: Schematic diagram of the continuous oxygen-liquid segmented flow setup used to prepare the feroxyhyte nanoflakes.

Synthesis of Carbon Nanodots

Mate herb was selected as carbon precursor. The plants were dried out and ground prior to a calcination step at 300 ºC for 2 h in air. The resulting solid was re-suspended in ultrapure water and centrifuged at 6,000 rpm for 10 min to remove large aggregates. The final suspension with a brownish yellow color contained the carbon nanodots and was stored at room temperature.

Synthesis of δ-FeOOH Nanoflakes/Carbon Nanodots hybrids

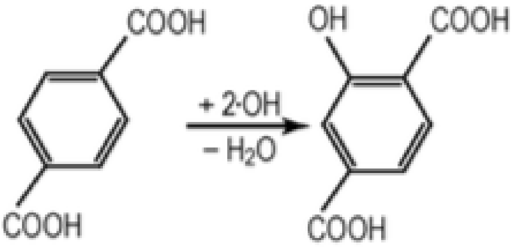
Fe-NFs/CNDs hybrids were assembled via a drying-vacuum step at low temperature. Typically, 0.2 g Fe-NFs were suspended in a mixture of 1 mL CNDs (0.5 mg/mL) and 1 mL deionized water, and stirred vigorously for 30 min. Then, the suspension was dried at 65 ºC in a vacuum-driven oven during 60 min.

Photo-Fenton catalytic experiments

The Photo-Fenton like activity was evaluated by measuring the decomposition rate of methyl orange (MO) in aqueous solution in the presence of two different LEDs (LED ENGIN, LZ4 models) emitting either at 532 nm (10 W) or 740 nm (6.3 W), respectively. In a typical reaction for decoloration, 0.6 mg of catalyst was dispersed in 3 mL of MO solution (25 mM). Prior to irradiation with LEDs, the suspension was magnetically stirred in the dark for 30 minutes to ensure the establishment of an adsoption/desortion equilibrium, followed by addition of H_2O_2 (2 mM). Different aliquots were taken at selected time intervals and analyzed by UV-Vis spectroscopy (V-67, Jasco Company) after retrieval of the catalyst. The experiments were performed at different pH values for systematic comparison.

Detection of hydroxyl radicals

The generation of hydroxyl radicals (·OH) during the Fenton-like process under LED illumination was monitored with the aid of terephthalic acid (TA). TA can generate a fluorescent derivative (2-hydroxy-terephthalic acid: HTA) emitting at ca. 425 nm after reacting with hydroxyl radicals according to the following reaction:



Scheme S1: Reaction of the non-fluorescent terephthalic acid probe with hydroxyl OH radicals to yield a fluorescent derivative emitting at 425 nm.

In a typical experiment, 0.6 mg of catalyst was dispersed in the probe solution containing TA (3 mL, 5 mM, pH at 4.8 or re-adjusted at 7.9 with NaOH) and deposited in a cuvette with 1 cm path length. Prior to irradiation with LEDs, the suspension was magnetically stirred in the dark for 30 minutes followed by addition of H_2O_2 (2 mM). Different aliquots were taken after selected irradiation time intervals and analyzed by fluorescence spectroscopy without retrieval of the catalyst. The experiments were performed at pH > 4 values to ensure the stability of the HTA fluorescent derivative.

Additionally, a set of experiments with the presence of increasing concentrations of methanol (a well-known hydroxyl radical scavenger) was also carried out for the most favorable conditions (pH = 2.8; LED visible; Fe-NF/CND hybrid). Different volumetric ratios MeOH:H_2O (0:1 / 0.25:0.75 / 0.5: 0.5) were tested under our photocatalytic decoloration conditions in order to evaluate the inhibition of the dye decoloration in the presence of increasing amounts of methanol.

Characterization techniques

The morphologies and particle size distributions were determined with the aid of a T20-FEI microscope with a LaB_6 electron source. Aberration corrected scanning transmission electron microscope images were additionally acquired using a high angle annular dark field detector (STEM-HAADF) in a FEI XFEG TITAN electron microscope operated at 80 kV equipped with a CETCOR Cs-probe corrector and an electron-dispersive spectroscopy (EDS) detector for elemental analysis. At least 200 particles were measured to evaluate the mean diameter of the particles and size distribution. To prepare the sample, the nanoparticle suspension was diluted with water prior to casting on a holey carbon TEM grid. The absorbance spectra of the different nanoparticles and the decoloration of methyl orange (MO) were monitored in a UV-visible-NIR spectrophotometer (V-67, Jasco Company) with a quartz cell of 1 cm light path. Samples were previously filtered through 0.2 μm Millex nylon membrane filters from Millipore. The determination of band gap energies was carried out assuming direct transitions (n) and plotting the following equation: $(\alpha h\nu) = A\ (h\nu\text{-}E_g)^{n/2}$ where α, h, ν, A and E_g represent the absorption coefficient, Planck´s constant, light frequency, proportionality constant and band gap energy, respectively. Fluorescence measurements were performed using a LS55 Fluorescence Spectrometer (PerkinElmer) equipped with a xenon arc lamp as the light source and a quartz cell (10 x 10 mm). Iron leaching experiments under acidic conditions were quantified by Microwave Plasma-Atomic Emission Spectrometer (Agilent 4100 MP-AES). The samples (2.5 mL) were digested with 1 mL of an acidic mixture containing $HCl:HNO_3$ (3:1 volumetric ratios) at 65 ºC for 2 h. The digested suspension was diluted with Milli-Q water to a final volume of 5 mL for spectrometric analysis. No traces of leached ionic iron were detected above the threshold detection limit of the equipment (0.05 ppm). The magnetic properties of the different nanoparticles were measured as dried powders after solvent evaporation at different temperatures in a superconducting quantum interference device (SQUID MPMS-5S, Quantum Design) from 0 to 40000 Oe. The samples were measured in a gelatin capsule (a diamagnetic correction for the sample holder was carried out). Magnetic hysteresis loops (plot of the magnetization of the sample as a function of the magnetic field strength) were evaluated at 37 °C.

Additional Figures

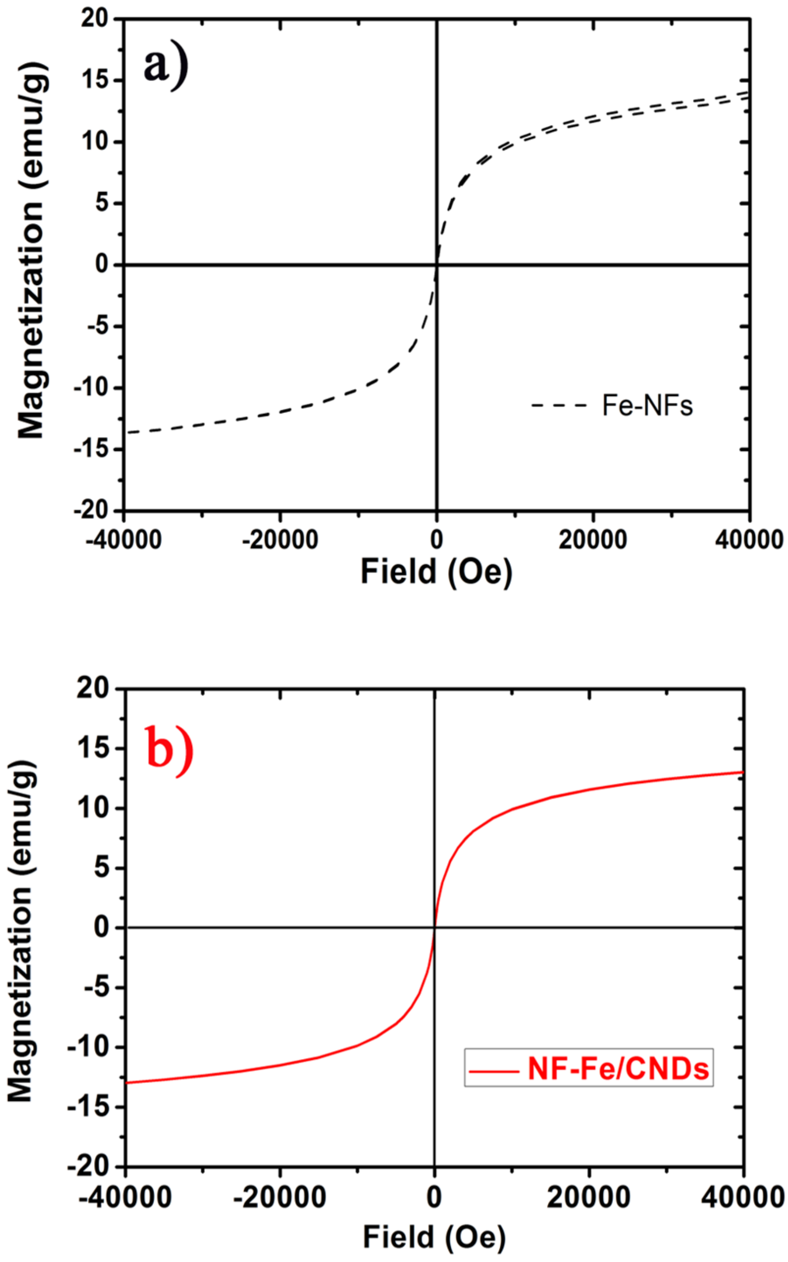


Figure S2. Magnetization curves corresponding to: a) the feroxyhyte nanoflakes and b) the composite photocatalyst measured at 37 ºC.

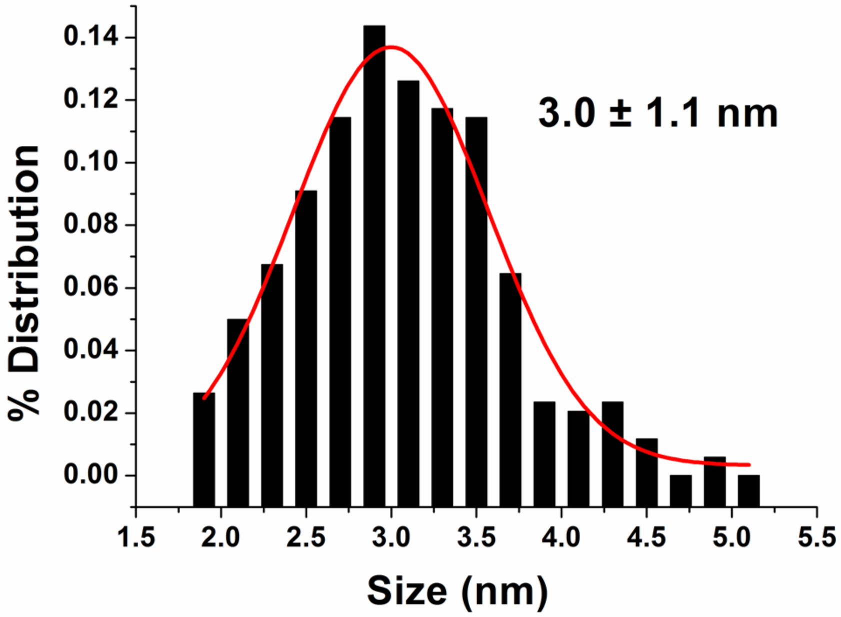


Figure S3. Particle size distribution of carbon nanodots after purification

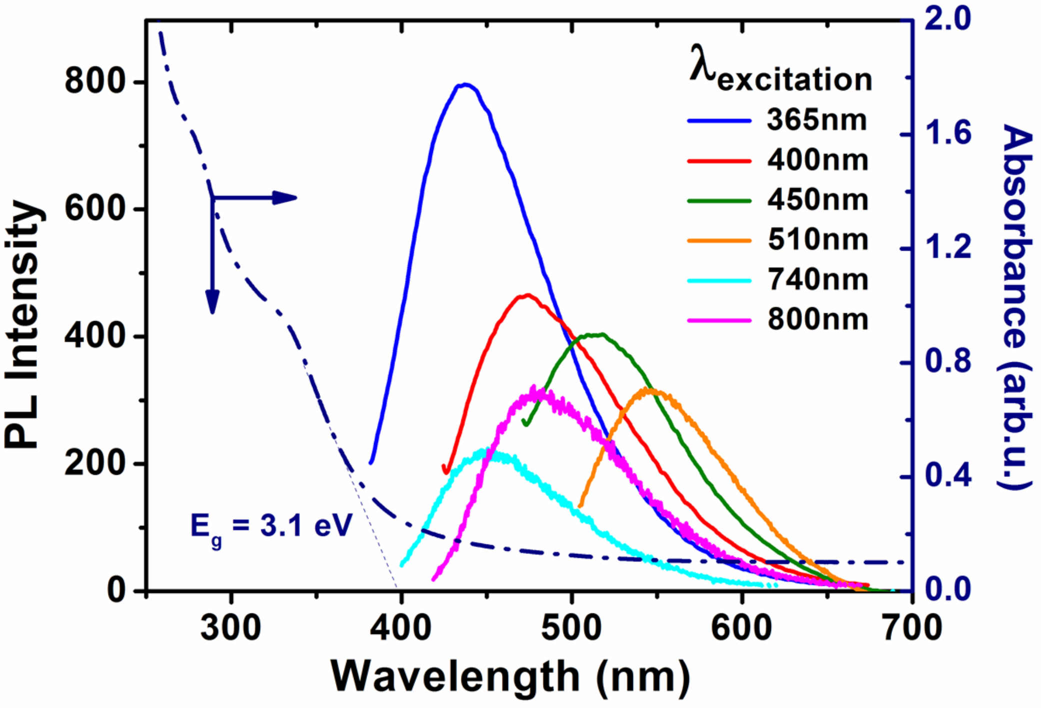


Figure S4. UV-Vis absorbance spectrum and Photoluminescence spectra acquired at room temperature in DI-H_2O at different excitation wavelengths corresponding to the upconverting carbon dots. Band gap energy is determined from the extrapolation of the absorbance spectrum. Note that the absorption spectrum does not decay totally and a fraction extends throughout the whole visible range.

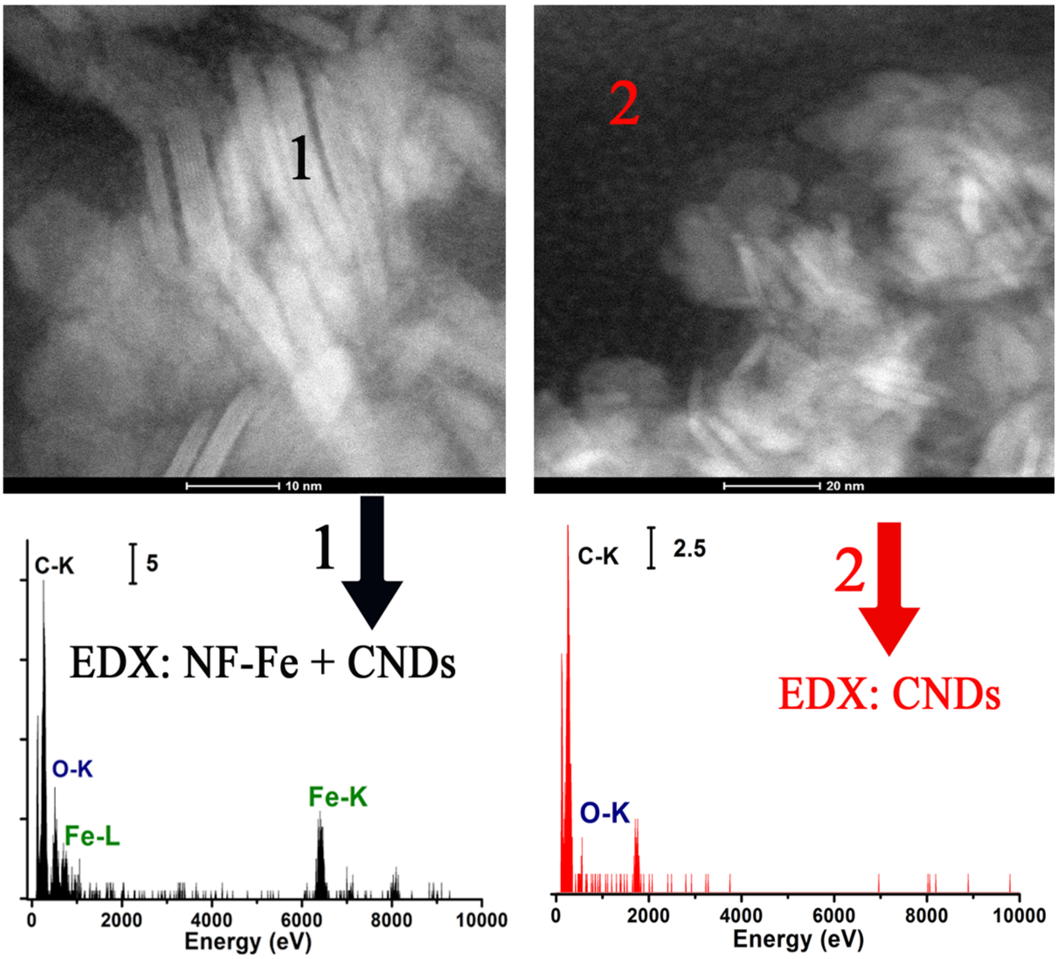
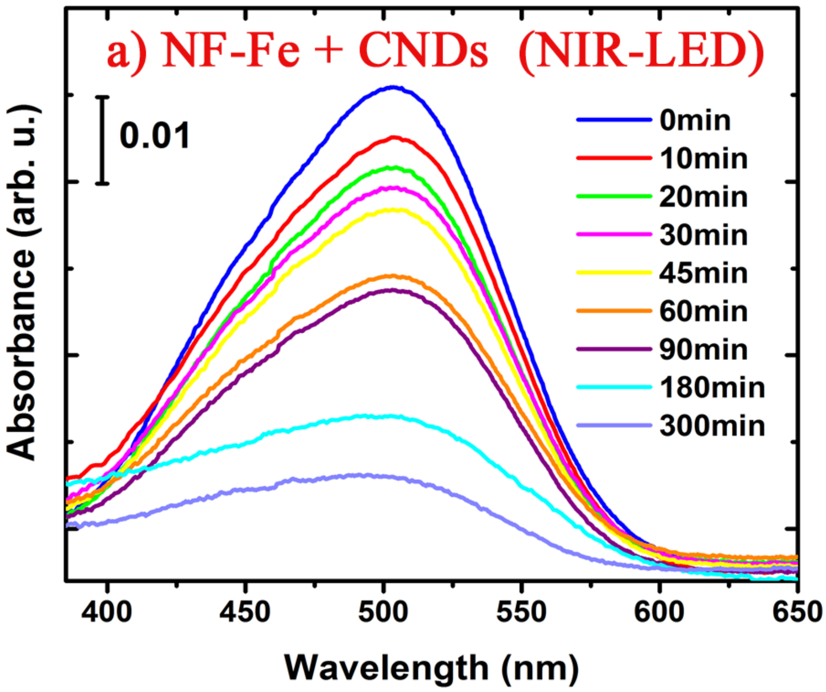


Figure S5. STEM images of the NF-Fe/CNDs composites and EDS analysis corresponding to different areas where CNDs are isolated (spot 2) or in the presence of the Fe-NFs (spot 1).



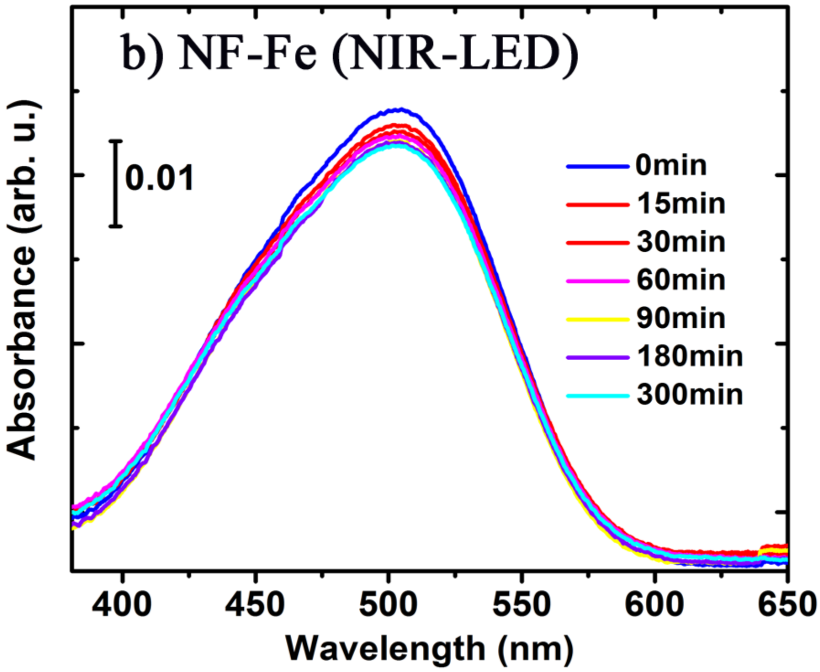


Figure S6. UV-Vis absorption spectra of the MO decoloration induced after different irradiation times under the NIR-LED source: a) in the presence of the NF-Fe/CND composite and b) in the presence of the NF-Fe only.

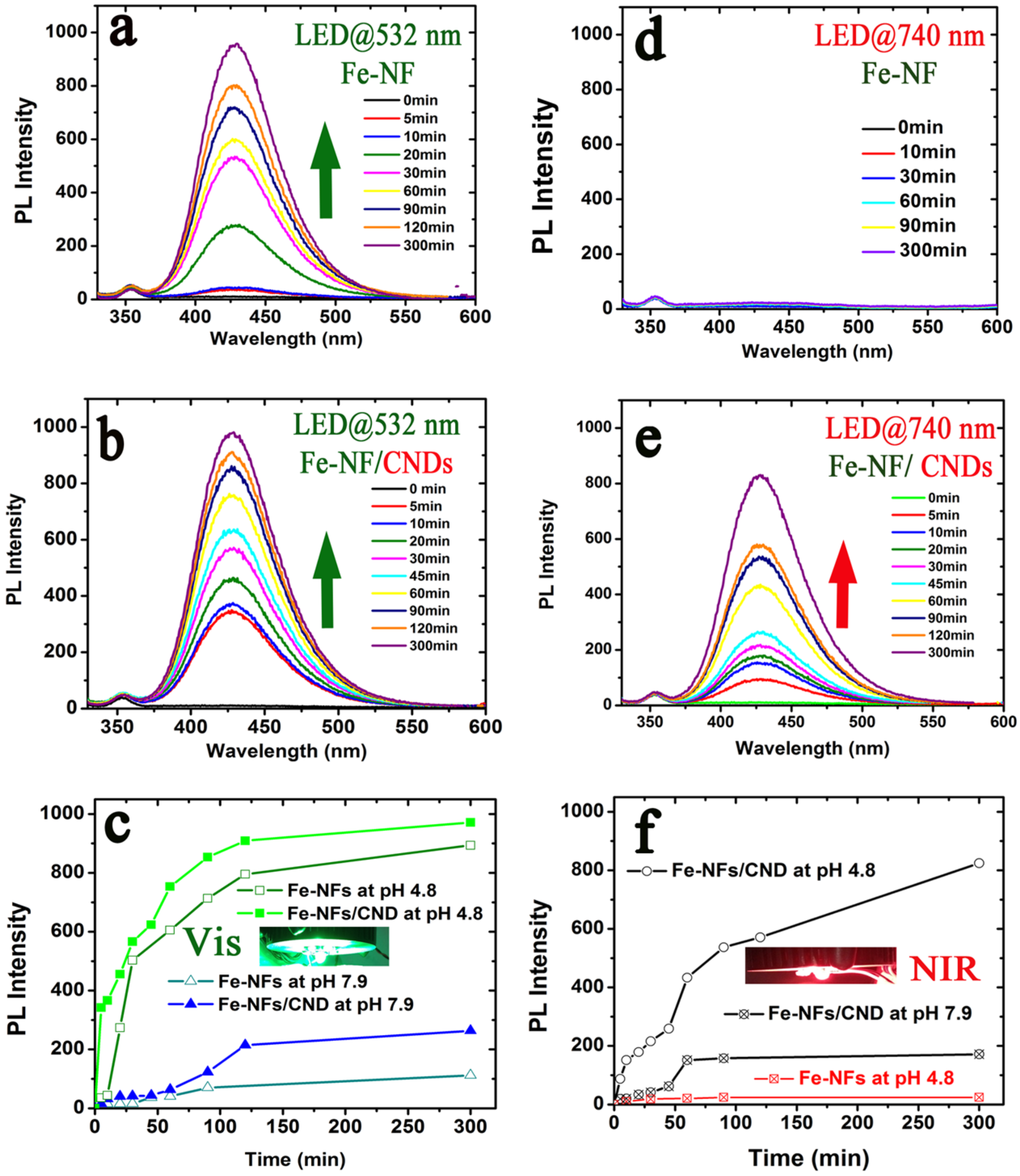


Figure S7. Direct quantification of ·OH radicals formation using terephthalic acid as fluorescent probe that emits in the presence of hydroxyl radicals according to the reaction shown in the Scheme S1; a-b) Fluorescence emission spectra of the terephtalate derivative formed upon different irradiation times under the visible LED at 532 nm and pH = 4.8 for the feroxyhyte nanoflakes and the composite with CNDs, respectively; c) Fluorescence intensity vs time curves corresponding to the experiments carried out at different pH values and the LED-Visible; d-e) Fluorescence emission spectra of the terephtalate derivative formed upon different irradiation times under the NIR-LED at 740 nm and pH = 4.8 for the feroxyhyte nanoflakes and the composite with CNDs, respectively; f) Overview of the evolution of fluorescence intensity vs time corresponding to the experiments carried out at different pH values and the NIR-LED. [MO] = 25 mM; [H_2O_2] = 2 mM.

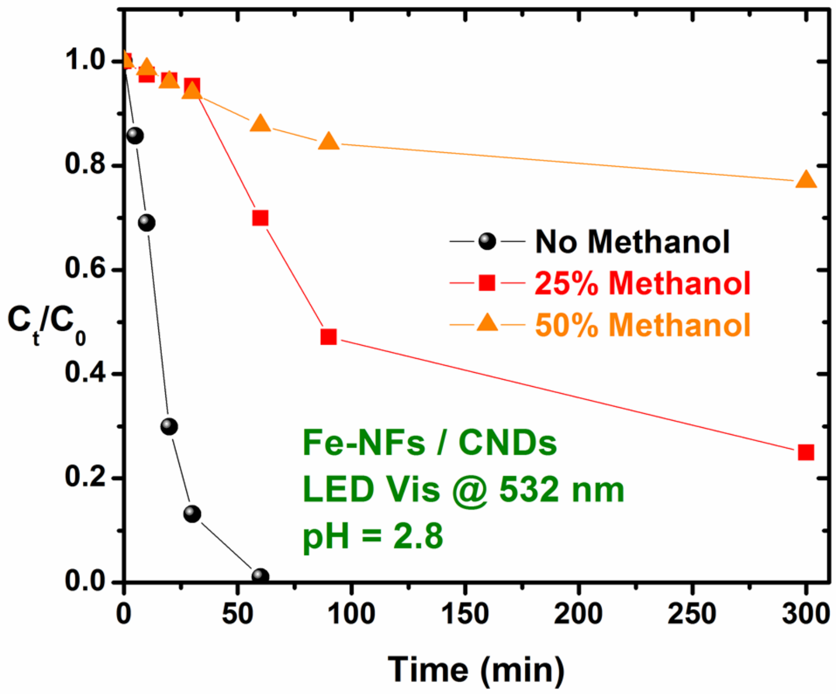


Figure S8. Evaluation of the scavenging effect of increasing amounts of methanol (expressed in % vol. respect to water) on the decoloration of MO using the feroxyhyte/CND composite at pH = 2.8 and under irradiation with the green LED. [MO] = 25 mM; [H_2O_2] = 2 mM.

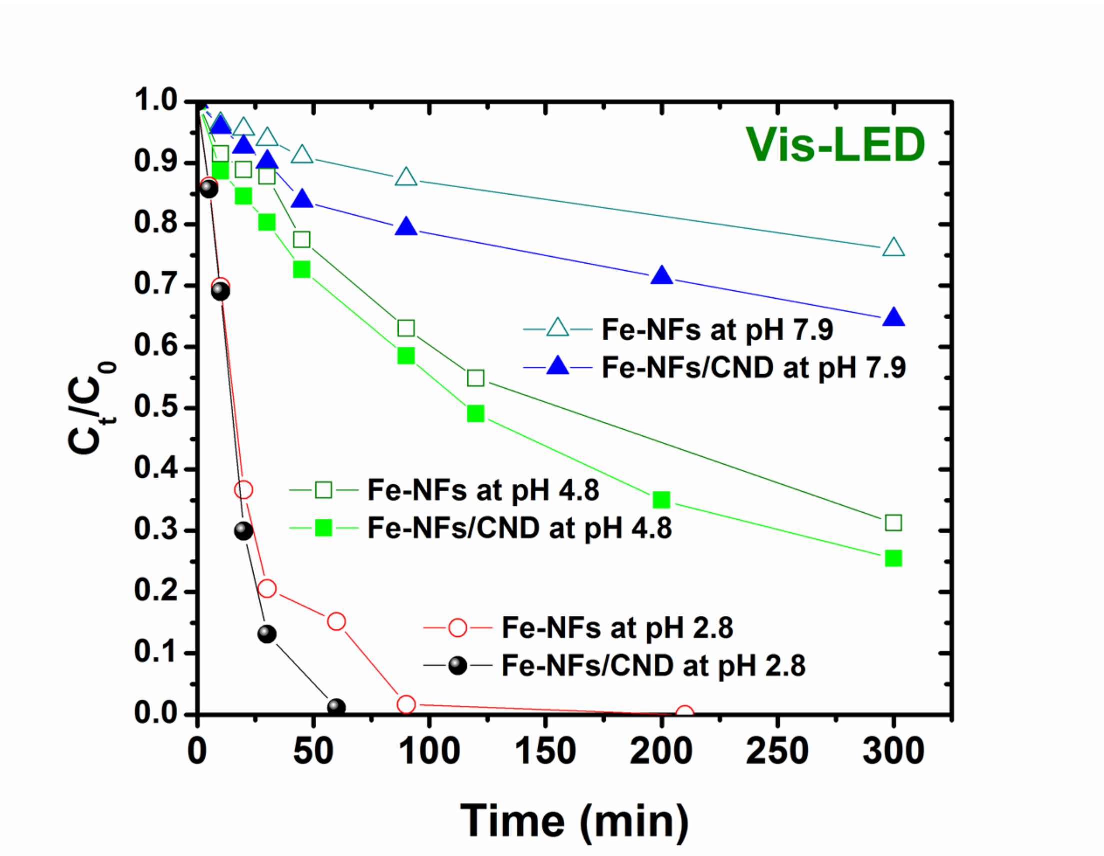


Figure S9. Effect of pH on the decoloration of MO using a 532 nm green LED in the presence of Fe-NFs/CNDs hybrids and Fe-NFs, respectively.

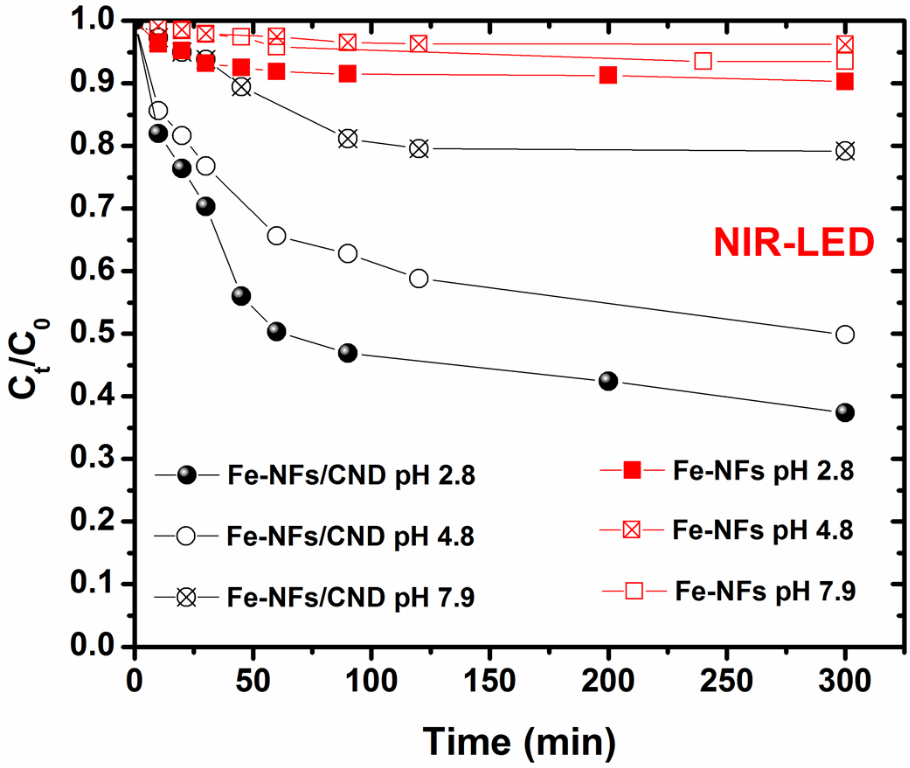


Figure S10. Effect of pH on the decoloration of MO using a 740 nm red-emitting LED in the presence of Fe-NFs/CNDs hybrids and Fe-NFs, respectively.

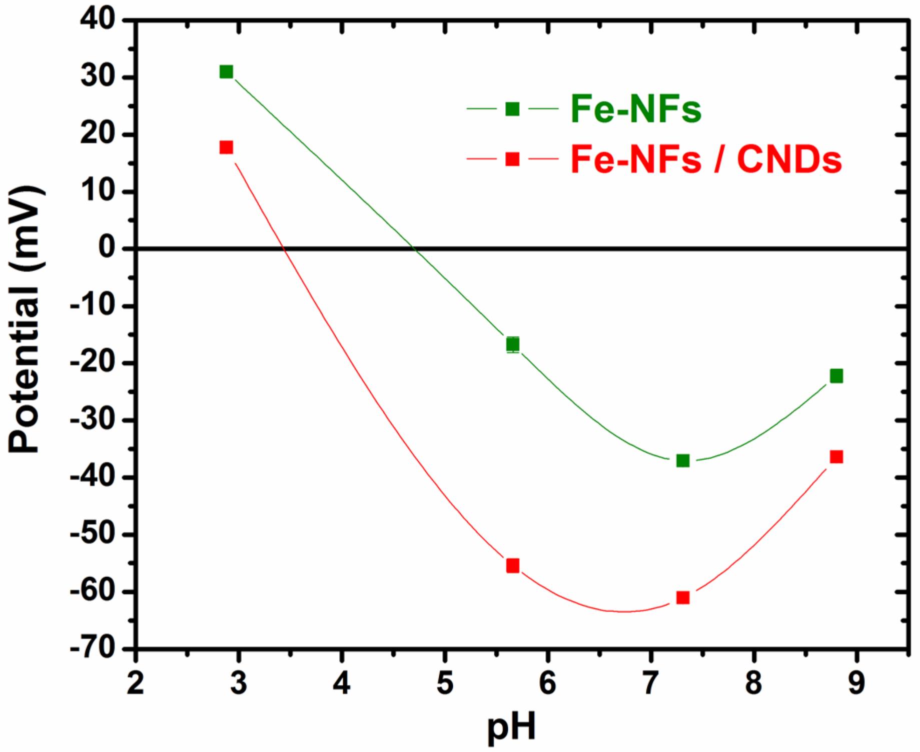


Figure S11. ζ-potential values of the feroxyhyte nanoflakes, the carbon nanodots and the Fenton-like composite catalyst at different pH.

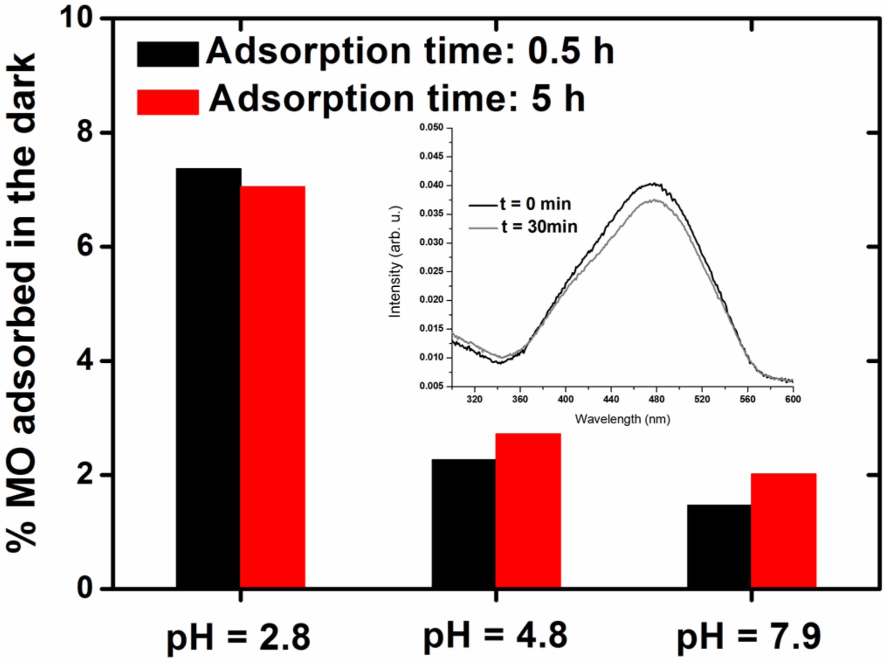


Figure S12. Influence of pH values and adsorption times on the amount of methyl orange adsorbed in the dark by the NF-Fe/CND composite. The inset corresponds to the adsorption carried out at pH = 2.8 after 30 minutes in the dark. The initial concentration of MO was 25 mM.

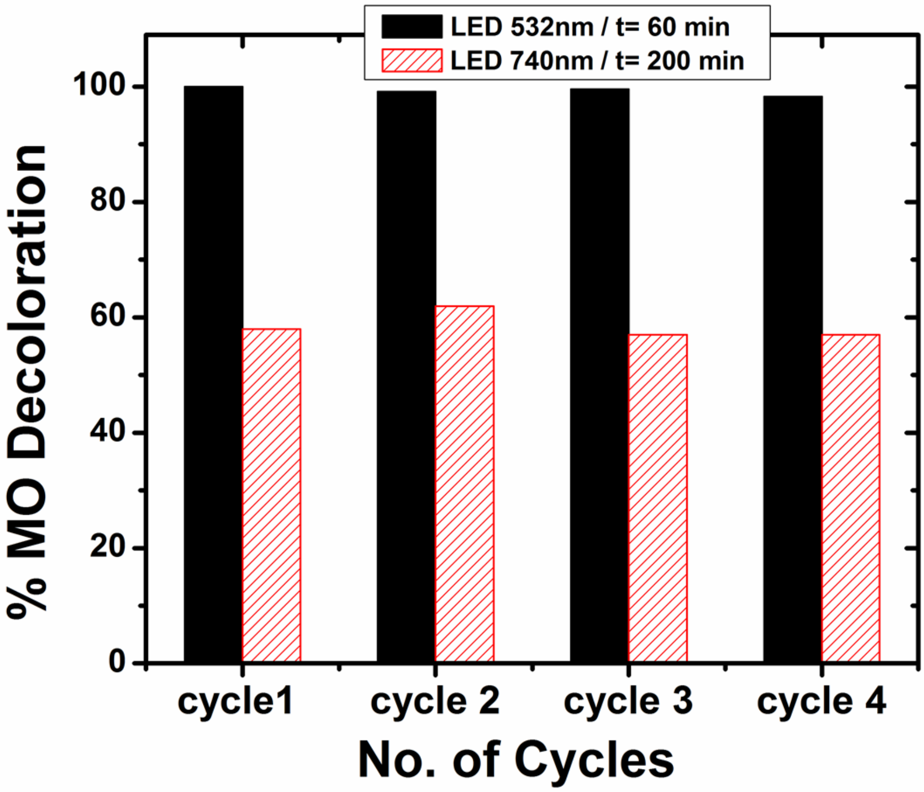


Figure S13. Recyclability of the Fe-NFs/CNDs hybrids after magnetic recovery