Supporting Information

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Hydrothermal synthesis of α-FeOOH (1D) nanorods and their transition to α-Fe$_2$O$_3$ (0D): An efficient photocatalyst in neutralizing hazardous organic dyes

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1. Experimentation

1.1 Chemicals and reagents

Ferric chloride hexahydrate (FeCl$_3$ .6H$_2$O), cetyl trimethylammonium bromide (CTAB), sodium hydroxide (NaOH), brilliant green (BG) and rhodamine B (Rh B) dyes were purchased from Sigma Aldrich, Mumbai (India). All chemicals were of AR grade and used without further purification. Distilled water was used throughout the experimentation.

2. Characterization

The crystal structure of α-FeOOH nanorods synthesis transition to α-Fe$_2$O$_3$ nanoparticles was determined using an X-ray diffractometer (CuKα λ = 1.5418 Å, diffraction angle (2θ) - 10 to 90 ^{o}, Shimadzu, Maxima 7000 S, Tokyo, Japan) at a scanning rate of 5° min^{-1}. The mean particle size was calculated using Debye Scherer's equation. The obtained data were compared with the standard JCPDS sheet. The Fourier transform infrared (FTIR, Perkin- Elmer Frontier spectrometer, United Kingdom) spectra were used to detect functional groups in α-FeOOH nanorods and α-Fe$_2$O$_3$ nanoparticles at a scanning range of 400–4000 cm^{-1}. UV–Vis absorption spectrum was noted using a UV–Vis spectrophotometer (Shimadzu UV 2450). A Photoluminescence (PL) spectrum was recorded using a photoluminescence spectrophotometer (Shimadzu RF 5300) in a quartz cuvette of 1 cm path length at room temperature. By using the identical N$_2$ adsorption-desorption isotherm,

"Brunner-Emmett-Teller (BET) investigations were undertaken to compute surface area, and Barret-Joyner-Halenda (BJH) analyses were performed to analyze pore size distribution study (Quantachrome Instruments). X-ray photoelectron spectroscopy (XPS) data were obtained using monochromatic aluminum with an Al Kα (1486.6 eV) with a source operating at a vacuum of 10^{-7} Pa. Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) was conducted from 30 °C to 900 °C (heating rate, 5 °C/min) under a nitrogen atmosphere using (Shimadzu DTG-60). LCMS analysis was conducted by (Thermo Fischer Scientific) Q- Plus Orbitrap. Dynamic light scattering (DLS) and Zeta potential were recorded using Malvern Zetasizer Nano ZS (ZEN 3600). The morphology and particle size of the nanoparticles were investigated (FESEM, Carl Zeiss SMT AG, Germany). EDAX (energy dispersive atomic X-ray analysis) was utilized for elemental analysis (Bruker instrument). Transmission electron microscope (TEM, JEM-2100) instrument was used for particle size measurements" [1]

3. Photocatalytic study

Dye degradation properties of α-FeOOH nanorods and α-Fe$_2$O$_3$ nanoparticles were studied towards the primary organic pollutant dyes (BG and Rh B). The dye solution was used at 10 ppm (10 mg dye/L deionized water). The degradation of dyes was examined using natural sunlight. The 50 ml dye solution was dispersed with 5 mg of α-FeOOH nanorods to achieve a concentration of 1.0×10^{-5} M. A small volume of the sample solution was examined by UV-Vis spectroscopy after a fixed interval of time, followed by the investigation of its adsorption-desorption equilibrium using the reaction mixture stirred for 30 min in dark conditions and then exposed to pure sunlight to assess the degradation behavior. The following equation measured the dye degradation efficiency.

$$Degradation\ (\%) = (1 - \frac{C}{C_0}) \text{ X } 100 \dots\dots\dots\dots\dots \ (5)$$

Where C_o is the concentration of the dye in water before irradiation, C is the concentration of the dye in water after a specific irradiation time. The Langmuir-Hinshelwood model is used to calculate the rate constant of the reaction

$$ln\frac{C_0}{C} = K_{app}\,t \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (6)$$

A pseudo-first-order kinetic rate constant at time t, called K_{app}, corresponds to the C_o initial dye concentration, and C is the final dye concentration after exposure to light. The experiment was repeated for four consecutive cycles to determine the reusability of the α-FeOOH nanorods and α-Fe$_2$O$_3$ nanoparticles.

4. Zeta potential

Zeta potential measurements have been conducted to determine the surface charge on as-synthesized α-FeOOH nanorods and α-Fe2O3 nanoparticles. Generally, zeta potential is used to analyze biomolecular stability and nanoparticle interactions. **Figure S1** shows the surface charges with zeta potentials ranging from -12 to -12.8 mV and -21 to -21.3 of α-FeOOH and α-Fe$_2$O$_3$, respectively. The zeta potential indicates that the samples are stable.
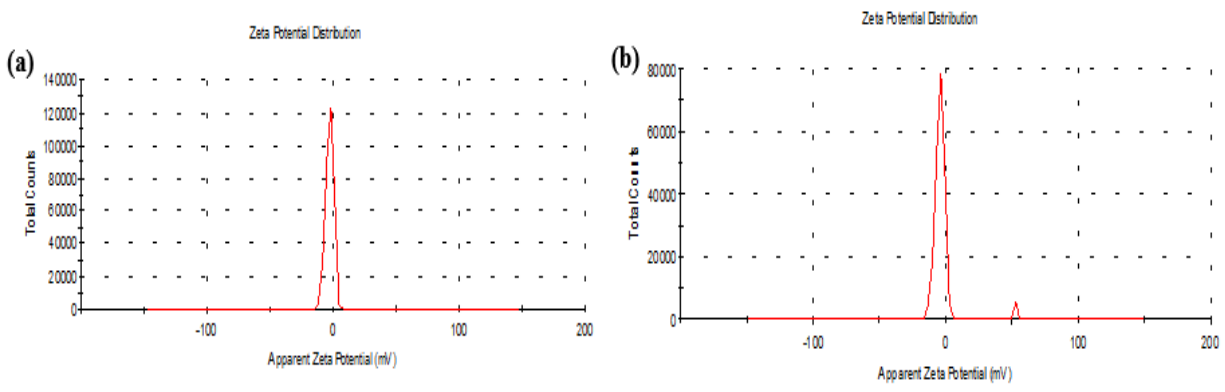

Figure S1 Zeta potential of α-FeOOH nanorods (a) and α-Fe$_2$O$_3$ nanoparticles (b)
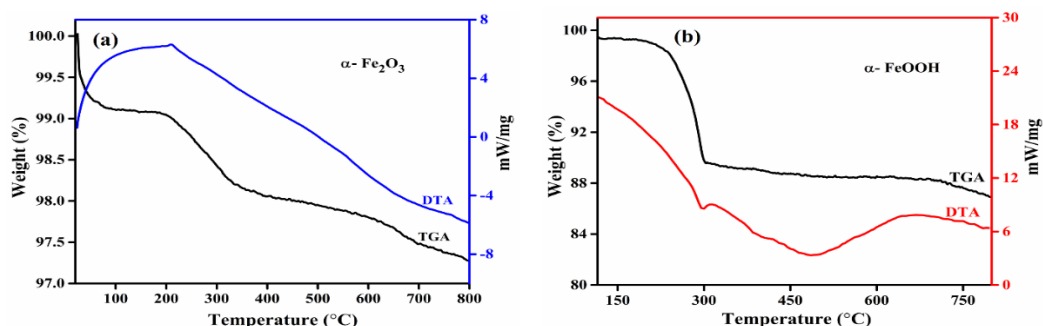
5. Thermal studies

Figure S2 TGA and DTA curve of α-FeOOH nanorods and α-Fe$_2$O$_3$ nanoparticles

Figure S2 (a-b) shows the α-FeOOH nanorods and α-Fe$_2$O$_3$ nanoparticles are studied under the nitrogen atmosphere with a range of temperatures from 30 °C to 800 °C to examine their thermal stability. α-Fe$_2$O$_3$ nanoparticles, the total weight loss for the synthesized α-Fe$_2$O$_3$ was about 3% which can be attributed to the removal of organic compounds. DTA peak was observed at 200 °C, as shown in **Figure S2 (a)**. Therefore the analysis confirms that the as-synthesized nanomaterial is thermally stable. The total weight loss for the synthesized α-FeOOH nanorods was about 12%. Water molecules evaporate from the surface of α-FeOOH nanorods at 150-300 °C. In addition, the sample shows a weight loss of 1% in the range of 300-800 °C, which can be attributed to the removal of organic compounds. DTA peaks were observed at 305 °C and 650 °C, as shown in **Figure S2** (b). Therefore the analysis confirms that the as-synthesized nanomaterial is thermally stable.

6. LCMS Analysis

LCMS analysis was utilized to look for potential degradation routes and intermediates [1]. The m/z peak at 474.9, equivalent to a brilliant green dye in **Figure S3(a)**, is shown here. Degradation of dye molecules (m/z = 62.0, 134.8, 224.9, and 431.6), as seen in **Figure S3(b)**, the processes of hydrolysis, hydroxylation, and decarbonization result in the formation of smaller molecules or ions. The hypothesized degradation pathways for BG are shown in **Figure S3(c)**, and the degradation processes for RhB are identical to those for BG. In **Figure S4(a)**, the m/z peak at 481.3 indicates the presence of the rhodamine B dye. **Figure S4(b)** also shows the degradation products' peaks after being in the environment (m/z = 62.0, 135.0, 270.7, and 341.7). The many routes of degradation are depicted in **Figure S4(c)**. Small molecules can also be obtained via oxidation (such as CO_2, H_2O, carbonylation, hydroxylation, dehydroxylation, and dehydrogenation)[2]
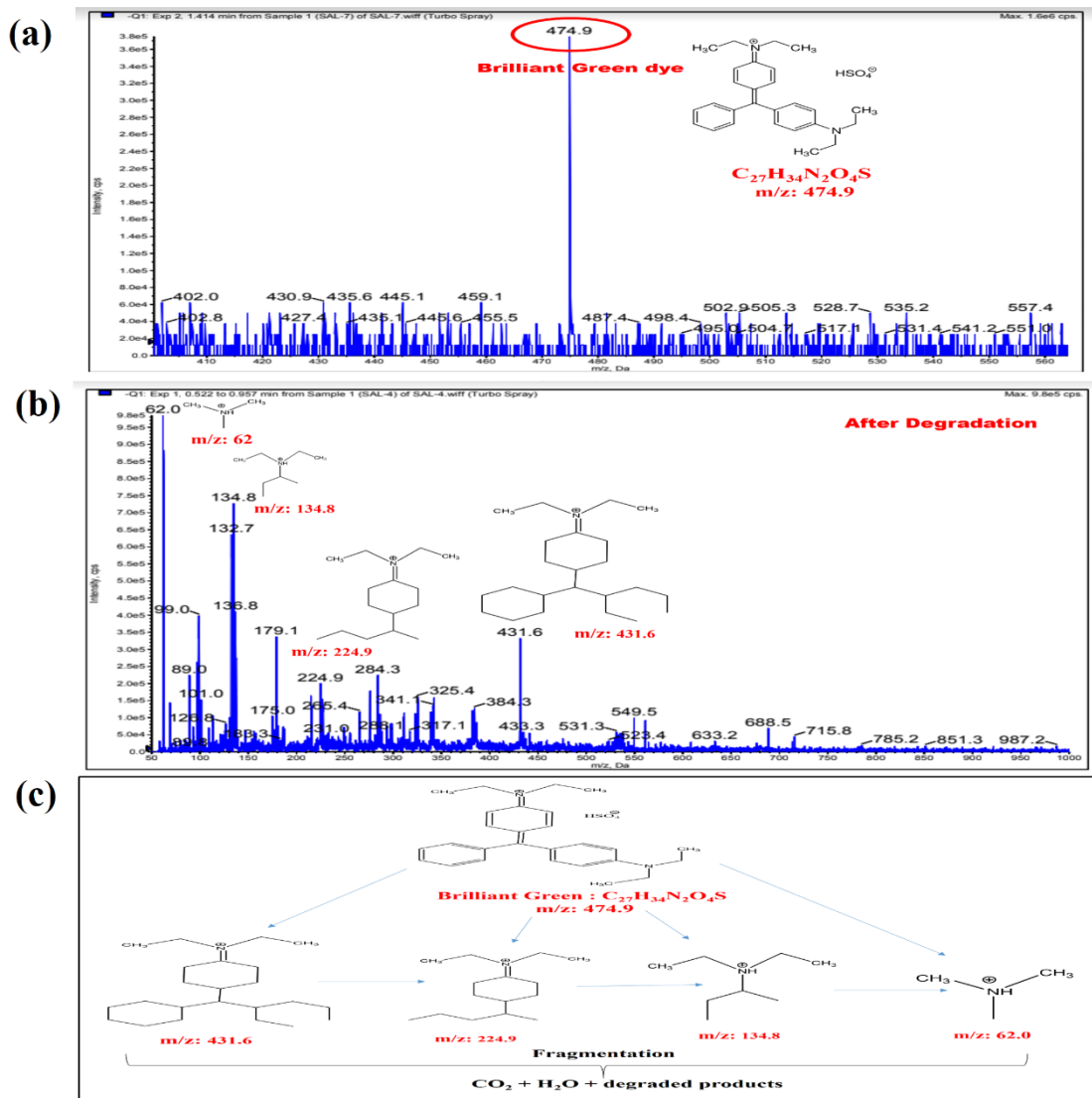
Figure S3 (a-b) LCMS of BG dye (before and after degradation) using α-Fe$_2$O$_3$ nanoparticles (**c**) proposed degradation pathways
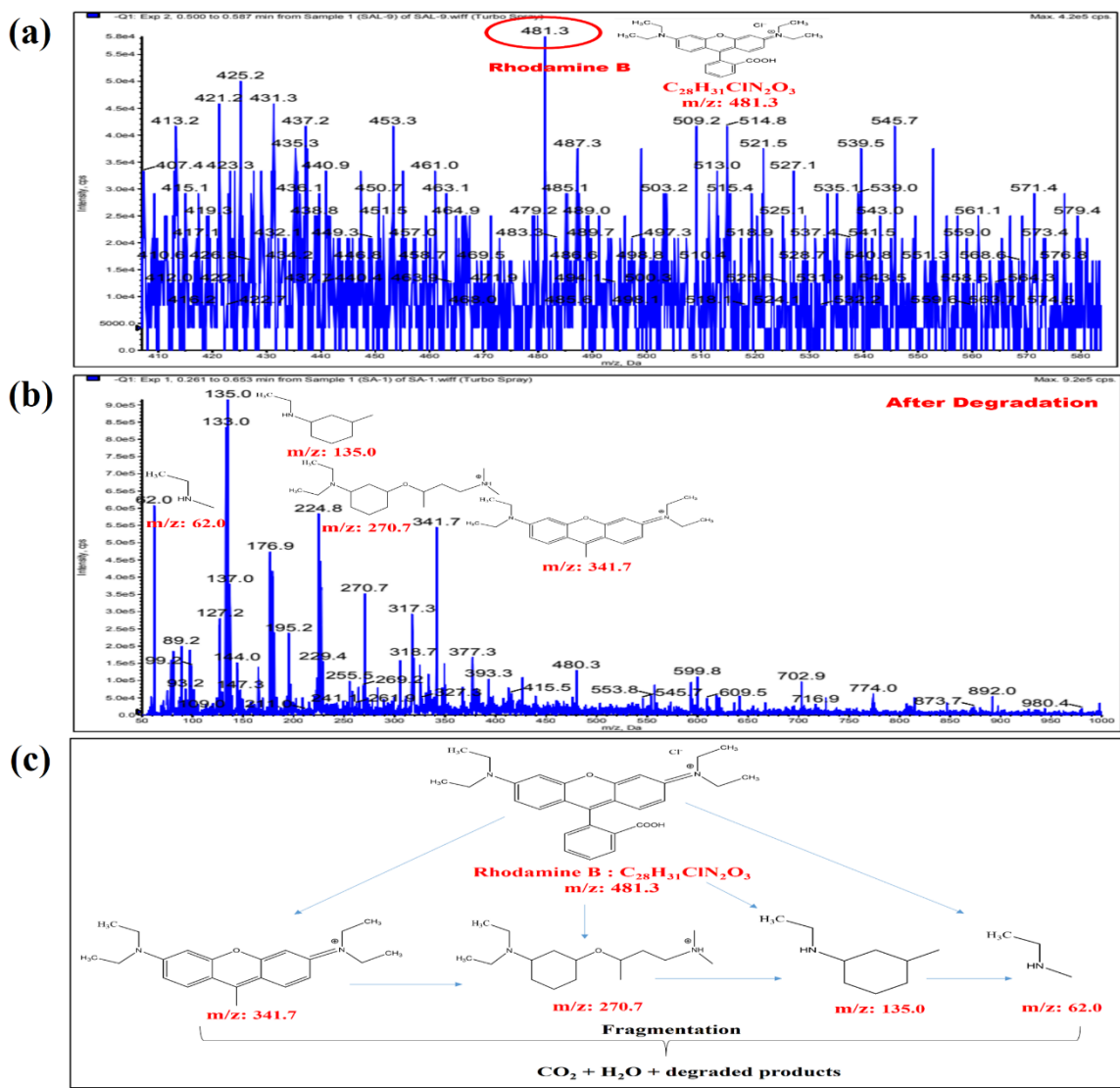
Figure S4 (a-b) LCMS of RhB dye (before and after degradation) using α-Fe$_2$O$_3$ nanoparticles **(c)** proposed degradation pathways

References

1   A. M. Sudapalli and N. G. Shimpi, *Opt. Mater. (Amst).*, 2022, **132**, 112849.

2   X. Liu, Z. Yang and L. Zhang, *J. Hazard. Mater.*, 2021, **403**, 123566.