Counter Anion-Directed Growth of Iron Oxide Nanorods in a Polyol Medium with Efficient Peroxidase-Mimicking Activity for Degradation of Dyes in Contaminated Water

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INTRODUCTION

Iron oxides (Fe₃O₄ or Fe₂O₃) are one of the most abundant and important minerals on earth. Considering the vast technological applications of these materials in their nanometer dimension, development of synthetic methods with control over size and shape is crucial. A size- and shape-dependent magnetic behavior along with biocompatibility of iron oxide nanoparticles has been harnessed for applications in areas such as ferrofluids, heterogeneous catalysis, magnetic recording media, removal of toxic elements (e.g., As, Pb, and Hg) from water, and several biomedical applications (e.g., gene therapy, immunoassay, contrast enhancement in magnetic resonance imaging, tissue repair, cell sorting, targeted drug delivery for diseases such as cancer, hyperthermia, and DNA separation). Various shapes like nanorods, cubes, rings, nanospindles, and hollow particles have been reported using this method. Therefore, there has been a great emphasis on the shape-selective growth of self-assembled ordered micrometer size iron oxide superstructures from an assembly of nanocrystals that ensures higher surface area, resulting in enhanced catalytic activity.

Several techniques have been adopted for the development of shape-selective iron oxides that include mechanochemical (electrodeposition, pyrolysis, laser ablation, combustion, etc.) and chemical (sol-gel synthesis, temperature-assisted synthesis, hydrothermal, microwave, reverse micelle, etc.) methods. The hydrothermal methods are especially attractive for tuning the morphological properties, including shape and size, of the magnetic superstructures with high aspect ratio. On the other hand, microwave methods provide a rapid and sustainable synthetic method in a cyclohexane-water-pentanol reaction medium.
using a variety of iron precursors having different solubilities. The polyl method of synthesis, which involves ethylene glycol as a solvent as well as stabilizing agent, has evolved as a soft chemical method for the preparation of a large variety of metal and metal oxide nanomaterials with tunable size, shape, and composition. However, the role of counterions in the precursor metal salts on the shape-selective growth of nanomaterials has not been understood clearly. It is recognized that during the growth the inorganic anions themselves might be selectively adsorbed on particular facets and thus greatly impact the final morphology. Therefore, it might be possible to obtain shape-selective iron oxides by varying the precursor metal salts in a polyl-based synthesis without using any external templates.

Iron oxide nanomaterials can be used as a low-cost and biocompatible alternative to the natural peroxidases, which are prone to loss of activation in a harsh chemical environment. Studies of the structural effects of these materials on their enzyme-mimetic behavior may be of high significance in designing materials for practical utility. In this direction, we studied the evolution of self-assembled iron oxide nano/microparticles with different morphologies using a polyl-based microwave synthetic method just by varying the metal salts (Scheme 1). Further, we evaluated the peroxidase-mimicking activity of the iron oxides and have observed significant enhancement in the nanozyme activity in the case of rod-shaped superstructures originated in the presence of NO$_3^-$ as counter anions. Taking advantage of the enhanced peroxidase mimetic behavior of these materials, we have utilized these materials for swift degradation of commercial dyes through a heterogeneous Fenton process that involves the generation of hydroxyl radicals (·OH) by the reaction of hydrogen peroxide and nanoscale iron oxide for the effective destruction of dyes. Overall, a rapid polyl-based microwave-assisted synthetic method has been developed for the generation of shape-selective Fe$_3$O$_4$ microstructures, which shows enhanced nanozyme activity and can be harnessed for effective degradation of organic contaminants.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Fe$_3$O$_4$ Microrods.

Self-assembled Fe$_3$O$_4$ microrods were synthesized via a simple microwave-assisted pathway using Fe(III) nitrate as the iron precursor and a mixture of PEG-200–water (PEG:water = 9:1 v/v) as the solvent at 150 °C for 60 min. It is well known that shape-selective synthesis of metal or metal oxide nanoparticles usually requires external templates, which dictates the oriented growth of the crystallites; however, in the present case, the shape selectivity leading to the formation of Fe$_3$O$_4$ microrods could be achieved simply by microwave heating of the metal salt in the polyl medium. The dark brown precipitates thus obtained were analyzed by various spectroscopic and microscopic tools. Scanning electron microscopy (FESEM) studies confirmed the formation of the rod-shaped microcrystals having dimensions of 800 nm width and 3–6 μm length (Figures 1a and S1). However, clusters of small nanocrystals of an average diameter of 10 ± 5 nm were found decorating the microcrystal surface. The results suggest that small Fe$_3$O$_4$ nanoparticles were probably assembled and grown directionally to form the microparticles.

Transmission electron microscopy (TEM) studies also suggested the formation of the Fe$_3$O$_4$ microrods having similar dimensions as obtained from the FESEM studies. Ultrasmall nanoparticles randomly adhering to the microcrystals were clearly visible in the TEM images (Figure 1b). The HRTEM image of the nanoparticles bound on the microcrystal surface showed lattice fringes with interplanar spacing of 0.25 nm that can be attributed to the (311) atomic plane of magnetite (inset: Figure 1b). Furthermore, the elemental mapping of the microrods reveals the existence of Fe, O, and C in the matrix and all of these three components are spread homogeneously in the microrod framework (Figure 1c). Energy dispersive x-ray spectroscopy (EDX) studies also validated the presence of carbon along with Fe and O in the matrix (Figure S2).

The phase characteristics of the microparticles were obtained from X-ray diffraction (XRD) patterns shown in Figure 2a. Diffraction peaks at 2θ of 18.3, 30.1, 35.5, 43.1, 57.0, and 62.6 could be perfectly indexed to spinal Fe$_3$O$_4$ and correspond to (111), (220), (311), (400), (511), and (440) lattices, respectively (JCPDS no. 65-3107). Interestingly, a

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**Scheme 1. Schematic Representation of Counter Anion-Dependent Evolution of Variable Shaped Iron Oxides via a Polyl-Based Microwave-Assisted Method**

![Scheme 1](https://example.com/scheme1.png)

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**Figure 1.** (a) Scanning electron microscopy (FESEM) image, (b) TEM image (scale bar 1 μm) of Fe$_3$O$_4$ microrods; inset: HRTEM image of nanoparticles decorated on the microrod (scale bar 5 nm), and (c) Elemental mapping of Fe$_3$O$_4$ microrods obtained under microwave condition at 150 °C for 60 min in a water–PEG mixture (1:9) using nitrate salt as a precursor.
The Fe$_3$O$_4$ phase. A small satellite peak at 719.0 eV coinciding with lattice oxygen, carbonyl oxygen, and alkoxo oxygen in Fe$_3$O$_4$ microrods, respectively. (Figure S3c).$^{52}$ The magnetic property of the Fe$_3$O$_4$ microparticles was investigated using a SQUID magnetometer (Figure 2d). The $M$−$H$ curve of the as-prepared material showed zero magnetic coercivity at 300 K, depicting a super-paramagnetic behavior. The saturation magnetization value was found to be 48 emu g$^{-1}$, which is lower than reported values for bare Fe$_3$O$_4$ nanoparticles. The reduced $M_s$ value of the microparticles might be attributed to the interaction of disordered amorphous carbonaceous layers with the Fe$_3$O$_4$ surface.$^{53}$

The molecular orientation and local bonding environments of the synthesized Fe$_3$O$_4$ particles were further confirmed by FTIR spectroscopy (Figure S4). The FTIR spectrum showed major vibrational peaks at 3440, 2928, 2360, 1628, 1053, 782, and 631 cm$^{-1}$, which can be owing to the vibrational modes of $ν$(O-H stretching), $ν$(-CH$_2$), $ν$(-C-H), $ν$(C=C stretching), $ν$(C=O stretching), $ν$(C-O stretching), $μ$(O-H bending), and $ν$(Fe-O), respectively.$^{54,55}$ Further, two prominent peaks at 1427 and 1354 cm$^{-1}$ were observed, which might arise due to the formation of mono or bidentate complex of carboxylic group of the carbon layer with surface Fe atoms.$^{56}$ The results suggested that the Fe$_3$O$_4$ surface was surface-passivated by a carbonyl-functionalized carbon layer. This was further evident in the $ζ$ potential measurement of the synthesized materials, which showed a value of $-21.3$ mV, as compared to a value of $+15.2$ mV for a bare Fe$_3$O$_4$ nanoparticle (synthesized through the well-known coprecipitation method using a mixture of Fe$^{2+}$ and Fe$^{3+}$ salts and NaOH under a N$_2$ atmosphere in water).$^{57}$

Thermogravimetric analysis (TGA) was employed to investigate the thermal stability of the synthesized material. As shown in Figure S5, a weight loss of 3−4% up to 150 °C could be attributed to the removal of the physically absorbed water. There was further weight loss of 16% probably due to the elimination of functional groups containing labile oxygen from the surface.$^{41,58}$ The N$_2$ isotherm, as shown in Figure S6, possesses the type IV isotherm with a small hysteresis loop in the 0.4−1.0 $P/P_0$ range, signifying the existence of mesopores. The Brunauer−Emmett−Teller (BET) surface area was calculated to be 62.0 m$^2$ g$^{-1}$, and the pore-size distribution from desorption analysis by the Barrett−Joyner−Halenda method was found to be 3.7 nm. Comparing to the small surface area of Fe$_3$O$_4$ nanoparticles,$^{55}$ the composite has significantly enhanced surface area, which might be due to the presence of a mesoporous carbon layer on the surface.

**Growth Mechanism.** The polyol method, which involves the use of poly(ethylene glycol) as both a reducing and stabilizing agent, is a well-known strategy for the growth of metal and metal oxide nanoparticles, where the nucleation and growth of the nanocrystals can be achieved with desired thermodynamic and kinetic control leading to self-assembled nanostructures. Shape selectivity of the nanocrystals is usually achieved by additional shape-directing agents, which are adsorbed preferentially on specific crystallographic planes, resulting in the change of direction and rate of crystal growth. Although the role of various additives on the stability of crystallographic planes is elaborately studied, there are only a handful of reports elucidating the influence of inorganic counterions in shape-selective growth of metal oxide nanoparticles without the involvement of external agents.$^{60,61}$
For the synthesis of the shape-selective Fe₃O₄ microrods, efficient and controlled heating provided by microwave irradiation was used in a tightly sealed closed vessel and the growth of the microrods was observed using Fe(NO₃)₃ as the starting precursor. Due to the fast kinetics of the nano-crystallite synthesis, it was not possible to elucidate a growth mechanism from time-dependent studies, as the microrod formation was observed even after 15 min of microwave heating (Figure 3a). However, the decoration of small Fe₃O₄ nanoparticles on the microrods clearly suggests that small nanocrystallites were initially formed, which gradually self-assembled into a microrod over time. Further, controlled experiments revealed that the amount of water in the solvent mixture played a significant role in the self-assembly process. No Fe₃O₄ nanoparticle assemblies were obtained without water injection. Whereas microrod formation occurred predominantly at a water-to-PEG ratio of 1:9 in the solvent mixture, only a few microrod formations were observed at a water-to-PEG ratio of 1:1. On the other hand, only nanospheres were formed when the water-to-PEG ratio was maintained at 9:1 (Figure S7). The results clearly infer the role of PEG in the self-assembly process.

Sealed vessel microwave processing allows rapid heating of the reaction mixture, allowing quick occurrence of the nucleation event relieving the solution supersaturation. Further growth of the initially formed nucleates takes place in a high and constant energy (Ostwald ripening). Along with their use as a high surface area catalyst, metal oxide nanoparticles have many promising applications, such as catalysis, gas adsorption, and photovoltaics. The formation of Fe₃O₄ microrods involves. When we performed the microwave synthesis at 80 °C keeping all other conditions similar, we obtained a cluster of nanoparticles after 5 min of microwave heating. SEM studies showed the formation of nanoparticles having dimension of 40 ± 10 nm in diameter (Figure S8). X-ray powder diffraction study revealed that the obtained nanoparticles had tetragonal FeOOH (β-FeOOH) structure (Figure S9). From these studies, we believe that the formation of the Fe₃O₄ microrods took place via β-FeOOH nanoparticle intermediates. Thus a plausible formation mechanism can be suggested as

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\text{Fe}^{3+} \rightarrow \text{Fe(H}_2\text{O})_6^{3+} \rightarrow \beta-\text{FeOOH} \rightarrow \text{Fe}_3\text{O}_4
\]

In an aqua-PEG mixture, the initially formed iron aqua complex undergoes dehydration to generate FeOOH nuclei under a microwave treatment. A combination of coarsening and oriented self-aggregation of the initially formed embryos leads to the growth of larger crystals with shape selectivity largely controlled by the Ostwald ripening process. A phase transformation occurred after an extended reaction period. The presence of PEG as a mild reducing agent ensures the reduction of Fe⁵⁺ to Fe³⁺, thus resulting in the formation of Fe₃O₄ microrods. It can be clearly observed that the Fe₃O₄ microrods consist of smaller Fe₃O₄ particles as building blocks and have irregular surface, demonstrating that the Fe₃O₄ nanoparticles self-assemble into the microrods (Figure 3b).

It was interesting to note that the self-assembled growth of Fe₃O₄ nanoparticles into one-dimensional microrods occurred without the addition of any shape-selective agents. We assumed that the NO₃⁻ counterions might play a critical role in the shape evolution. Therefore, we varied the metal salt precursors in the microwave-assisted polyol process, while keeping all reaction parameters, such as concentration of the metal salt, water-to-PEG ratio, reaction temperature, etc. constant. When FeCl₃ was used as the precursor metal salt, hollow Fe₃O₄ microparticles with an average diameter of 1.1 ± 0.1 μm were obtained. SEM studies (Figure 4a) reveal the surface configuration of the microspheres, which is not smooth, implying that these microspheres are comprised of small nanoparticles as primary building units and self-assembled to form the larger near spherical aggregates. The formation of internal voids in the microspheres can be clearly seen in the XRD spectra (Figure 4b). All diffraction peaks in the hollow microsphere powder XRD spectra (Figure 4b) could be indexed to the α-Fe₂O₃ hexagonal phase (JCPDS card no. 33-664). Considering the oxidative etching properties of the halide ions, the formation of the complex hollow assemblies with a different phase could be easily understood. When iron acetate was used as the precursor metal salt, only...
small spherical Fe₃O₄ nanoparticles with an average dimension of 40 ± 10 nm were obtained. Acetates are known to have high binding affinity for oxide surfaces and hence act as an efficient stabilizer restricting the growth to smaller dimensions. (Figure 4c). The results suggest that the inorganic anions from the precursor salts were influential in controlling the size, shape, and structural evolution of the micro/nanoparticles.

It is well-known that during the crystallization process, the inorganic anions might selectively adhere on particular facets. The FeOOH nucleates initially obtained are stabilized by PEG molecules through chelation, thus suppressing the nucleation and growth of nanocrystals in the solution. The aggregation of formed nuclei takes place to eliminate the interfaces and minimize the total energy of the system. NO₃⁻ ions are known to have different adsorption strengths on different crystal facets, which might cause faster growth of nanocrystals in the direction with weaker adsorption. Although the exact mechanism for the microrod morphology could not be traced, we believe that a combination of both anion facet coating and stabilization of adatoms by PEG was crucial for growth of various superstructures. This was further confirmed by the fact that when Fe(NO₃)₃ was hydrothermally treated in a Teflon-sealed autoclave using a PEG–water mixture as a solvent at 180 °C for 12 h, the resultant precipitate consisted of Fe₃O₄ microrods with an average diameter of 0.5–0.7 μm and several micrometers of length with a much smoother surface as compared with the microwave-based method (Figure 4d). The formation of the graphitic layer on the nanoparticle surface could be realized as the microwave/hydrothermal treatment of PEG leads to the formation of carbonaceous materials.

**Oxidation of Peroxidase Substrates Catalyzed by Rod-Shaped Fe₃O₄ Microcrystals.** In recent years, the enzyme-mimetic activities of metal oxide nanoparticles have been pursued extensively. The natural enzymes are prone to deactivation if the reaction conditions such as pH of the medium or temperature are modulated to some extent. Due to their ease of synthesis, coupled with their stability under harsh reaction conditions, metal oxides are considered as an ideal alternative to natural enzymes for various applications. The peroxidase-mimicking activity of Fe₃O₄ nanoparticles is well studied, and there are reports on the enhancement of peroxidase activity depending on the shape of the nanocrystals. The catalytic oxidation of the 3,3,5,5′-tetramethylbenzidine (TMB) was carried out in the presence of H₂O₂, to assess the peroxidase-like activity of the Fe₃O₄ microrods, and the progress of the reaction was monitored via UV–visible
spectroscopy. As shown in Figure 5a, the colorless substrate TMB is oxidized in the presence of H$_2$O$_2$ and Fe$_3$O$_4$ microrods to a blue solution, with enhancement in absorption intensity at 430 and 652 nm. In the absence of H$_2$O$_2$, addition of only Fe$_3$O$_4$ microrod to TMB resulted in negligible color variation under similar experimental conditions. These results indicate that the Fe$_3$O$_4$ microrods demonstrate an efficient peroxidase-like behavior toward typical peroxidase substrates like TMB and a blue charge-transfer complex (chromogen) is formed quickly, catalyzed by the Fe$_3$O$_4$ microrods in presence of H$_2$O$_2$. To achieve an optimal response, the effects of pH on the catalytic activities of the Fe$_3$O$_4$ micrometrystals were investigated in a series of buffer at varying pH from 2 to 10. The response curves (Figure 5b) show that the maximum catalytic activity was obtained at pH 4.0, which is very similar to the operating conditions for horseradish peroxidase (HRP). To eliminate the role of any leached iron in the catalytic reaction, the iron contents of the supernatants after removal of the microrods by centrifugation were measured by inductively coupled plasma atomic emission spectroscopy and the amount of Fe ions was negligible in the pH range of 3–6. The catalytic activity of any leached iron ions was evaluated for the catalytic reaction at pH 4.0. For this, the Fe$_3$O$_4$ microrods were incubated in an acetate buffer at pH 4.0 for 30 min and the supernatant solution after removal of the microrods was used to monitor the oxidation of TMB. The original colorless solution remained colorless, confirming that no leached Fe ions were involved in the catalytic process, as the concentration of leached iron was much lower than the amount required for typical Fenton reactions. Thus, a 100 mM acetate buffer solution at pH 4.0 was selected as the optimal reaction medium for all subsequent studies.

The dependence of the peroxidase-mimicking activity of Fe$_3$O$_4$ microrods on various parameters, such as concentration of TMB and H$_2$O$_2$ and amount of the catalyst, was also carefully monitored by observing the absorption peak at 652 nm (Figure 5c,d). The maximum catalytic efficiency was achieved at 0.1 mM of TMB, whereas in the case of H$_2$O$_2$, a higher concentration of H$_2$O$_2$ was required to attain the maximum peroxidase-like activity. This indicates that the catalytic activity of the microrods is more prominent at high concentrations of H$_2$O$_2$ as compared with HRP. At higher concentration of TMB in the reaction medium, the peroxidase activity was weakened, probably due to sufficient catalytic surface capping at a particular concentration, thus inhibiting the attachment of excess substrates onto the surface. The maximum catalytic activity of the Fe$_3$O$_4$ microrods was achieved at a H$_2$O$_2$ concentration of 1000 mmol/mL, which is 10$^3$ times that of TMB. A catalyst concentration as low as 8 $\mu$g mL$^{-1}$ was used to monitor the kinetic parameters.

The steady-state kinetic assays were performed in the TMB-H$_2$O$_2$-Fe$_3$O$_4$ reaction system at room temperature, and the catalytic parameters were evaluated by correlating the absorbance data with the Michaelis–Menten equation (eqn).

\[
\nu = \frac{V_{\text{max}}}{K_m + [S]}
\]

where $K_m$ is the Michaelis constant and $\nu$, $V_{\text{max}}$ and [S] correspond to the rate of conversion, maximal velocity (or the maximal conversion rate), and substrate concentration, respectively.

A typical Michaelis–Menten kinetics model was validated during the TMB-H$_2$O$_2$ reaction catalyzed by the Fe$_3$O$_4$ microrods, as observed from the initial absorbance against time plots (Figure 5e,f). The slopes of these plots are evaluated as initial reaction rates at variable substrate concentrations. The catalytic parameters of $K_m$ and $V_{\text{max}}$ were obtained by plotting the reaction rate against concentration and following nonlinear regression using the Michaelis–Menten equation. The $K_m$ value of Fe$_3$O$_4$ microrods with TMB as a substrate was calculated to be 0.05 mM, which is significantly lower compared with the reported value of 3.7 mM in the case of native horseradish peroxidase. This indicates a stronger affinity of Fe$_3$O$_4$ microrods for TMB compared with HRP (Table S1). The higher peroxidase-like activity of the Fe$_3$O$_4$ microrods was consistent for H$_2$O$_2$ as a substrate also (0.09 mM), with a lower $K_m$ value. The high peroxidase activity of the microrods can be correlated to the presence of large number of Fe$^{2+}$ and Fe$^{3+}$ ions on their surface, compared with only one iron in HRP. For comparison, we also evaluated the peroxidase activity of Fe$_3$O$_4$ nanoparticles synthesized using Fe(OAc)$_3$ as a salt precursor and Fe$_2$O$_3$ hollow microparticles obtained using FeCl$_3$ as the precursor metal salt, using TMB as the substrate. From the plot of the reaction rate vs concentration of TMB and using the Michaelis–Menten kinetic model, $K_m$ values were calculated to be 0.15 and 0.31 mM for Fe$_3$O$_4$ nanoparticles and Fe$_2$O$_3$ hollow microparticles, respectively (Figure S10). From the results, it is evident that the Fe$_3$O$_4$ microrods showed superior peroxidase-mimicking activity for TMB, compared with the Fe$_3$O$_4$ nanoparticles or hollow Fe$_2$O$_3$ microparticles. The graphic layer on the Fe$_3$O$_4$ particles also might contribute to the enhanced peroxidase-mimicking activity of the microrods, as several carbonaceous nanomaterials are known to demonstrate peroxidase-mimicking properties.

It is well-established that peroxidase mimics catalyze the decomposition of H$_2$O$_2$, leading to efficient generation of...
hydroxyl radicals (·OH); therefore, a fluorescent probe was used to track the formation of ·OH radicals catalyzed by Fe₃O₄ microrods. The experiment was performed using weak fluorescent terephthalic acid as probe, which generates a highly fluorescent hydroxyl terephthalic acid as a product when reacted with ·OH radicals (Figure S11a). In the presence of Fe₃O₄ microrods and H₂O₂, the free radical generation was clearly evident, as exhibited by a dramatic increase in fluorescence (Figure 6b). As the reaction progressed, the fluorescence intensity of terephthalic acid enhanced at 440 nm. These results indicated that the peroxidase-mimicking activity of Fe₃O₄ microrods was mainly due to their potential to generate ·OH radicals during the course of reaction.

Kinetic Study of Pyrogallol. The peroxidase-mimicking activity of the as-obtained Fe₃O₄ microrods was further evaluated for the oxidation of pyrogallol in the presence of H₂O₂, which forms a yellow purpurogallin complex. Upon addition of Fe₃O₄ microcrystals (20 μg mL⁻¹) and H₂O₂ to a solution of pyrogallol in phosphate buffer (pH 7.4), the colorless solution turned yellow, with the appearance of a new absorption peak at 420 nm, signifying catalytic oxidation of the colorless solution turned yellow, with the appearance of a new absorption peak at 420 nm, signifying catalytic oxidation of the pyrogallol substrate (Figure S11a). The reaction was monitored at different time intervals by varying the concentration of pyrogallol and H₂O₂. The catalytic reaction was completed after 30 min, and the absorbance at 420 nm remained stable. The time-dependent formation of the purpurogallin complex was also monitored for the Fe₃O₄ nanoparticles and Fe₃O₄ hollow microparticles, which showed relatively lower catalytic activity compared with the Fe₃O₄ microrods (Figure S11b). Similar to TMB, the oxidation of pyrogallol also follows Michaelis–Menten kinetics. Studying the kinetics at variable pyrogallol concentrations and keeping the H₂O₂ concentration constant, a Lineweaver–Burk plot was obtained for catalysis using Fe₃O₄ microrods, which showed a linear relationship (Figure 7a,b). From the Lineweaver–Burk plot, the Michaelis–Menten constant Kₘ was evaluated. The calculated Kₘ value of 0.52 mM for pyrogallol is lower than that of the natural enzyme HRP (0.81 mM), indicating that the Fe₃O₄ catalysts have higher affinity toward the substrate. The Kₘ value was obtained from the Lineweaver–Burk plot at variable H₂O₂ concentrations, while keeping the pyrogallol concentration fixed at 17 mM.

Degradation of Dye Pollutants Using Fe₃O₄ as Catalyst. Organic dyes are predominantly used in several industries, such as photographic printing, textile, tannery, paper-pulp, and paints, and are mixed with soil and water, causing severe damage to the environment. To get rid of these hazardous pollutants, various processes, such as ozonation, chlorination, adsorption, ultrafiltration, electrochemical processes, photodegradation using photocatalysts, and advanced oxidation processes such as hydroxyl radical (·OH), which can be used for efficient removal of organic dye contaminants. However, due to low decomposition of H₂O₂ at room temperature, catalysts are often required for the sustained formation of ·OH radicals. A combination of nanocatalysts and H₂O₂ in a single process could function as an attractive substitute for dye removal.

Encouraged by the high peroxidase-mimicking activity of Fe₃O₄ microcrystals, we further examined the activity of Fe₃O₄ microrods for the degradation of common organic dyes. Considering the fact that the overall surface charge of the microcrystals was negative, we first studied the degradation of cationic rhodamine B as a model contaminant. The degradation of the dye was visually observed in a mixture of Fe₃O₄ catalyst, H₂O₂, and rhodamine B in aqueous medium, and complete decolorization occurred within 120 min at room temperature. The absorption of the dye gradually decreased with increasing Fe₃O₄ concentration, indicating that the dye degradation efficiency was highly dependent on the nanocatalyst concentration (Figure S12). To optimize the reaction conditions, a concentration-dependent study was performed by varying the concentration of H₂O₂ from 0–50 mM (Figure S13). At a lower concentration of H₂O₂, a slower degradation of rhodamine B was observed. As the concentration was increased to 50 mM, the rate of degradation increased, suggesting that a H₂O₂ concentration of 50 mM was optimal for dye degradation. Further, degradation of rhodamine B was studied at different pH. Figure S14 clearly shows that the maximum rhodamine degradation efficiency was found at pH 4, a similar pH range at which the maximum peroxidase activity was obtained. The quick degradation and a gradual reduction in the prominent absorption peak intensity at 553 nm were further observed during the time-dependent UV–visible spectroscopy studies. A linear correlation between the reaction time and ln(C₀/C) could be ascertained (Figure 8a), suggesting that a pseudo-first-order pathway was followed during the dye degradation reaction with a rate constant of 0.038 min⁻¹. Control reactions were performed in the absence of the catalyst or H₂O₂, and no initiation of the dye degradation occurred even after prolonged time, suggesting that a combination of Fe₃O₄ microcrystals and H₂O₂ was essential for the degradation reaction. The excellent performance of Fe₃O₄ microcrystals for the rhodamine B degradation could be ascribed to a combination of the high surface area of the microcrystals and efficient peroxidase activity.

From the time-dependent kinetics studies, it was apparent that no shift in the absorption maxima at 553 nm was observed in the initial 60 min (Figure 8b) and only a continuous reduction in the absorbance was observed. It has been reported that N-de-ethylation and cleavage of the chromophore are two competitive ways of degradation of rhodamine B, followed by other reactions, such as hydroxylation, aromatic ring opening, and mineralization. In the case of N-de-ethylation, auxochromatic properties of N-ethyl moieties lead to a hypsochromic shift in the absorption maxima. On the other hand, only a...
molecules near the Fe3O4/solution interface. H2O2 molecules are adsorbed on the surface and diﬀerent atoms. The •OH radicals then cleave the dyes adsorbed on the surface or diﬀuse into the solution to degrade the dye molecules near the Fe3O4/solution interface.

The degradation of other commonly used dyes, such as methylene blue (MB) and methyl orange (MO), was further monitored using the Fe3O4–H2O2 catalytic system to ascertain the scope of the present method in waste-water treatment (Figure 8c–e and S15). UV–visible spectroscopy studies were performed to monitor the decay in the concentrations of MB and MO in the solution by observing absorbance at λmax 663 and 463 nm, respectively. In comparison with the degradation of rhodamine B (degradation efficiency DE = 98% and k = 0.038 min−1), the degradation was moderate for MB (DE = 77% and k = 0.011 min−1) and MO (DE = 60% and k = 0.007 min−1), under similar reaction conditions (0.5 mg mL−1 of Fe3O4 microrods, 50 mmol L−1 of H2O2 and 0.1 mmol of dye after 2 h at room temperature). It is evident that RhB was degraded faster than MB, although they are both cationic in nature. The carboxyl group in rhodamine B might influence the formation hydroxyl radicals and facilitate their attack on the dye molecules through hydrogen bonding.77,78 MO is an anionic dye and possibly is slowly adsorbed on Fe3O4 surface due to the electrostatic repulsion, severely impacting its degradation.

Catalyst reusability and stability are regarded as important parameters for practical catalytic applications. We compared the dye removal activity of the fresh and recovered Fe3O4 catalysts toward RhB, and a catalyst concentration of 0.5 mg mL−1 was used. After every cycle, the catalyst is directly withdrawn from the solution by centrifugation followed by thorough washing and redispersed in distilled H2O for the next cycle of catalysis by adding RhB and H2O2. This catalyst retained good activity (82%) even after reuse ﬁve times, suggesting high stability of the catalyst even in the presence of a large amount of H2O2 (Figure 8f).

To verify whether Fe3O4 micro rods can be employed to treat environmental water, tap water and lake water were collected from an industrial area (Pithampur, Indore) and used as the practical sample (Figure S16). This was kept for some time and then ﬁltered before being spiked with rhodamine B as the model pollutant. When Fe3O4 micro rods and H2O2 were added to this dye containing water, effective discoloration of the solution occurred within a short time (90 min) due to the degradation of rhodamine B. Even in the lake water containing a mixture of dyes (rhodamine B, MO, and MB), the Fe3O4 micro rods could eﬀectively degrade all dyes in the presence of H2O2. Therefore, the Fe3O4 micro rods can be employed as a promising nanocatalyst for the environmental waste-water treatment.

**CONCLUSIONS**

A novel microwave-based synthetic methodology has been developed for the rapid self-assembled growth of Fe3O4 microrods using polyol method without the aid of any external shape-directing molecular templates. The growth of the size, shape, and morphology-selective micro/nanostructures was highly dependent on the iron precursor salt used for the synthesis, demonstrating the role of counterions in directing the growth mechanism. The microwave treatment of the iron...
precursors in a polyol medium also led to the growth of a thin carbonaceous layer on the Fe₃O₄ microcrystals. The Fe₃O₄ microcrystals showed excellent peroxidase-mimicking activity against substrates such as TMB and pyrogallol, demonstrating their high capability for applications in environmental remediation in presence of H₂O₂. This property was taken advantage of for the degradation of common organic pollutants, such as cationic and anionic dyes, with high efficiency. The method presents a simple, one-step synthesis of magnetic microcrystals with high stability (negligible iron leaching, no phase transformation after reaction), large surface area, and the possibility of magnetic separation, which can be harnessed for several other technological applications, such as degradation of other organic contaminants, photocatalysis, etc.

### EXPERIMENTAL SECTION

**Materials.** Fe(NO₃)₃·9H₂O, FeCl₃·3H₂O, and Fe-(C₂H₃O₂)₂ were purchased from TCI chemicals. Poly(ethylene glycol) 200 (PEG-200), methyl orange (MO), rhodamine B (RhB), methylene blue (MB), and terephthalic acid were obtained from Sigma-Aldrich. 3,3,5,5′-Tetramethylbenzidine (TMB), 1,2,3-trihydroxybenzene (Pyrogallol), and hydrogen peroxide (30%) were obtained from Sisco Research Laboratories (SRL), India. Sodium acetate trihydrate, acetic acid, and NaH₂PO₄ were purchased from Merck Ltd, India. Ultra-pure water obtained from the Milli-Q system was used in all experiments.

**Characterization.** UV−visible absorption spectra and kinetic studies were recorded at room temperature on a Varian UV−visible spectrophotometer (Carry 100 Bio). The infrared spectrum (IR) was recorded in a Bruker Tensor 27 FTIR spectrometer in the transmission mode using KBr pellets to prepare the samples. Powder X-ray diffraction spectra (XRD) of the as-prepared sample were measured by a Rigaku Smart lab X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm) in the range of 2θ of 10−80°. For transmission electron microscopy (SEM) studies, samples were prepared by dropcasting on a ITO surface and the images were recorded on a Supra 55 Zeiss apparatus with an energy dispersive X-ray (EDX) attachment. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded using a JEOL JEM-2100 microscope (accelerating voltage of 200 kV). To prepare the samples for TEM testing, the sample solutions were cast on the coated copper grid and dried at room temperature. Emission spectra were recorded using a fluoromax-4p fluorometer from Horiba (model FM-100). The CEM discover Microwave reactor was used for the synthesis of materials. A Raman spectrum was recorded using the Jobin Yvon Horiba LABRAM-HR micro Raman system with a 632.8 He-Ne laser beam attachment. Magnetic property was investigated using an Ever Cool 7 Tesla SQUID Magnetometer. The area surface assessment of Brunauer−Emmett−Teller (BET) was performed on Auto-sorb iQ, version 1.11 (Quantachrome Instruments). X-ray photoelectron spectroscopy (XPS) was performed using the Mg Kα radiation photoemission tool PHI 5000 Versa Prob II, FEI Inc.

**Synthesis of Fe₃O₄ Micro/Nanoparticles with Controlled Morphology.** Rod-shaped iron oxide microcrystals were obtained by dissolving Fe(NO₃)₃·9H₂O (196 mg, 80 mM) in a PEG-200−water mixture (PEG:water ratio 9:1, total volume 5 mL). The mixture was then transferred into a screw-mount glass tube and subjected to 150 W, 200 psi, and 150 °C microwave radiation for 60 min. This resulted in a dark brown dispersion of Fe₃O₄. The precipitate was cleaned with water and ethanol several times after cooling to eliminate impurities. For the synthesis of hollow microspheres and nanospheres, FeCl₃·3H₂O (80 mM) and Fe(C₂H₃O₂)₂ (80 mM) were used as iron precursors, respectively, keeping all other synthetic parameters similar. For the hydrothermal synthesis of Fe₃O₄ nanorods, Fe(NO₃)₃·9H₂O (80 mM) precursor salt was dissolved in 20 mL of the PEG-200−water mixture (the PEG:water ratio was 9:1 v/v) and was transferred in a Teflon-sealed autoclave, which was kept at 180 °C for 12 h.

**Peroxidase-Mimicking Activity Studies.** The peroxidase-like activity of the synthesized Fe₃O₄ microstructure was studied for the oxidation of TMB as a substrate. Kinetic experiments were conducted in time-dependent mode using a UV−visible spectrophotometer to monitor absorbance at 652 nm. Experiments were carried out using 20 μL of a Fe₃O₄ microrod stock solution (1 mg mL⁻¹) in a total volume of 2.5 mL of sodium acetate buffer solution (100 mM acetate buffer, pH 4.0). TMB (0.1 mM) was used as a substrate and H₂O₂ concentration was 4 mM, unless stated otherwise. The steady-state kinetic measurements were performed under the optimal reaction conditions by varying the TMB concentration from 0.01 to 0.2 mM at a fixed concentration of 4 mM H₂O₂. Similarly, the kinetic analysis of Fe₃O₄ with H₂O₂ as the substrate was performed by using a fixed concentration of 0.1 mM TMB and varying the amount of H₂O₂ (0.05−0.4 mM). The effect of pH (2−10), TMB concentration (0.01−0.5 mM), and H₂O₂ concentration (0.01−2.000 mM) on the catalytic activity of Fe₃O₄ microcrystals was also investigated.

The kinetic studies of pyrogallol oxidation were carried out in a pH 7.4 phosphate buffer solution at room temperature. The concentration of pyrogallol was varied while maintaining a constant amount of Fe₃O₄ catalyst (20 μg mL⁻¹) and H₂O₂ concentration (40 mM). The Michaelis–Menten constant (Kₘ) was calculated using Lineweaver–Burk plots of the double reciprocal of the Michaelis–Menten equation.

**Detection of Hydroxyl Radicals.** In a typical reaction process, 1.0 mg of Fe₃O₄ microrods was dispersed via sonication in 5.0 mL of sodium acetate buffer (pH 4.0) solution containing 50 mM H₂O₂, followed by addition of 1 mM terephthalic acid and 3 mM NaOH. After incubation, the suspension was centrifuged at different time intervals; at an excitation wavelength of 315 nm, the supernatant was collected for fluorescence measurement.

**Dye Degradation.** For the dye degradation studies, 0.5 mg mL⁻¹ Fe₃O₄ microrods were dispersed into 20 mL of rhodamine B stock solution (0.1 mmol L⁻¹) prepared in acetate buffer (pH 4.0). After preadsorption at room temperature for 5 min, the absorption of rhodamine B was measured by UV−visible spectroscopy and considered as C₀ (initial concentration). Addition of 50 mM H₂O₂ into the above solution initiated rapid catalytic degradation of rhodamine B. About 2.5 mL of the solution was taken out from the reaction mixture at an interval of 20 min, and the suspended Fe₃O₄ particles were removed either by centrifugation at 8000 rpm for 2 min or by magnetic separation. The absorption of the supernatants was recorded on a UV−visible spectrophotometer. Similarly, the dye removal efficiency of Fe₃O₄ microrods was investigated by time-dependent measurement of absorption maxima of MO (0.1 mM) and MB (0.1 mM) dyes in aqueous medium under similar reaction conditions. We
also examined the effect of pH, concentration of catalyst, and H₂O₂ concentration (0–50 mM) on the catalytic efficiency of dye degradation.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01201.

TGA spectrum, SEM images, FTIR spectrum, EDX spectrum, XRD spectrum, UV–visible spectra of dye reduction, XPS spectra, BET spectra, and experimental results in tabular form (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We acknowledge IIT Indore for the research infrastructure and SIC, IIT Indore for providing the instrumentation facilities. We are grateful to SAIF NEHU, Shillong for providing HRTEM facility, IIT Mumbai for TEM facility, UGC-DAE Consortium are grateful to SAIF NEHU, Shillong for providing HRTEM facility.

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