Supplementary Information (SI) for RSC Advances.

Supporting Information

High-efficiency RhB dye degradation using β-FeOOH nanorods via Tribocatalysis

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Materials and Chemicals:

All materials were utilized in their raw form without undergoing any purifying processes. The compounds $FeCl_3 \cdot 6H_2O$ and NaOH were purchased from Sinopharm Chemical Reagent CO., Ltd.

Synthesis of β-FeOOH

The β-FeOOH catalysts were synthesized via a hydrothermal route. The catalysts obtained were utilized without any prior treatment for dye degradation. The synthesis procedure was discussed in detail below: The precursor solution was prepared by dissolving 2 g of $FeCl_3 \cdot 6H_2O$ in 20 mL of deionized, and stirrer for about 30 minutes at room temperature. Subsequently, 2 g of NaOH was dissolved in an additional 20 mL of deionized water to form a solution. Afterward, the NaOH solution was slowly added to the previous solution and stirred for about 30 minutes at room temperature. Next, the solution was transferred into a 100 mL autoclave lined with Teflon and heated at different temperatures i.e. 80 ^oC, 100 ^oC, and 120 ^oC, for a period of 6 hours. After the reaction was completed, the resultant light-yellow catalyst was cooled to ambient temperature, and the samples were washed several times to remove the impurities. The final catalysts dried at 70 °C in a vacuum oven for about 24 hours. Finally, the obtained catalysts were denoted as β-FeOOH-80 ^oC. β-FeOOH-100 ^oC, and β-FeOOH-120 ^oC. The complete synthesis route is shown in the main manuscript Scheme 1. The pH of the RhB solutions was adjusted using dilute solutions of hydrochloric acid (HCl, 0.1 M) and sodium hydroxide (NaOH, 0.1 M). The pH was measured and confirmed using a calibrated digital pH meter (Model pH100b, Shanghai Haiker Environmental Protection Equipment Co., Ltd) prior to each tribocatalytic experiment.

Characterizations

XRD patterns of the β-FeOOH powder samples were obtained on a Rigaku Ultima IV diffractometer using Cu Kα radiation (λ = 0.15 418 nm) in the range of 10−60° with a step of 0.02°. The morphology and microstructure were investigated using scanning electron microscopy (SEM, ZEISS, Sigma 500) and transmission electron microscopy (TEM, JEOL JEM 2100F). XPS was used to determine elemental compositions, chemical states, and valence band position of catalysts (ThermoFisher Scientific, Escalab Xi^+ spectrometer). UV-vis diffuse reflectance spectra of powder samples and dye concentration of reaction solutions were measured on a UV-vis spectrophotometer (Shimadzu, UV-2450). BET surface area of the samples was obtained from the N_2 adsorption−desorption isotherm measured at 77 K using a Micromeritics TriStar 3000 system with prior outgassing at 120 °C for 12 h to desorb the impurities of moisture. Tribocurrent density-time curves were measured using an electrochemical workstation (CHI660E). A catalytic powder was prepared by dispersing the catalyst powder in a solvent with a Nafion binder, which was then drop-cast onto the nickel foam current collector and allowed to dry.

Tribocatalytic performance analysis

The tribocatalytic performance of the β-FeOOH catalysts was evaluated by the degradation of the RhB dye solution under ultrasonic vibration in the dark. In all tribocatalytic experiments, an ultrasonic cleaner (120 W, 40 kHz) was adopted to provide mechanical vibration to catalysts. In addition, the tribocatalytic performance of the catalyst was also investigated by RhB degradation under magnetic stirring in the dark. A magnetic stirrer with a rotation speed of 800 rotations per minute was used to provide a friction effect to the catalyst. Briefly, 0.05 g of freshly prepared FeOOH catalyst was dispersed in 50 mL of an aqueous RhB dye solution with a concentration of 5 mg/L. Prior to ultrasonic treatment, the suspension was stirred for 1 hour to establish adsorption–desorption equilibrium between the catalyst and dye molecules. The concentration of dye after

equilibration was denoted as the original concentration (C_0). Subsequently, a glass cup containing the mixture solution was put into the water-filled ultrasonic cleaner. To detect the reaction process, after every 10 min, 4 mL of the reaction solution was withdrawn and centrifuged to separate the catalyst, and the residual dye concentration (C) at any reaction time (t) was acquired using a UV-vis spectrophotometer and plotted as a function of reaction time. The percentage of residual concentration of dye was marked with (C/C_0). The catalysts after use were recollected and further used several times under the same experimental conditions to evaluate the cyclic stability. To measure the tribocurrent density the foam was cut into precise discs with a geometric area of X cm^2, then the tribocurrent density (J) was calculated using the formula J=I/A, where I is the measured tribocurrent (μA) and A is the projected geometric area (cm^2) of the catalyst-coated nickel foam electrode. The generation of •OH was identified using terephthalic acid as a molecule probably fluorescence photoluminescence spectra analysis using a fluorescence spectrophotometer (Cary Eclipse, Varian). The generation of $\bullet O_2^-$ was confirmed by the reduction of NBT. Typically, the β-FeOOH catalyst was dispersed in 25 mL of NBT (10 mg L^{-1}) solution in a beaker and then stirred for 15 min in the dark to achieve adsorption-desorption equilibria. After that, the beaker was put into an ultrasonic cleaner to start the catalysis reaction, 3 mL of suspension was collected every 10 min, and the NBT concentration was determined using UV-vis absorption spectra. Active species trapping experiments were carried out by adding BQ, TBA, and EDTA-2Na solutions into are action solution to scavenge $\bullet O_2^-$, •OH, e^-, and h^+, respectively. EPR spectra were measured to verify the generation of •OH and $\bullet O_2^-$ active radicals during tribocatalytic reactions. In the catalytic reaction process, circulating cooling water flowed through the ultrasonic cleaner to keep the stable water level, and the catalytic reaction temperature was maintained at ≈30 °C. The ultrasonic cleaner was covered with tin paper to keep a dark condition.

Quantitative analysis of H_2O_2

The quantitative detection of hydrogen peroxide generated during the catalytic process was accomplished using a colorimetric method with o-tolidine as the specific chemical indicator. Following a prescribed protocol, a sample of the reaction suspension was first centrifuged at 14,000 rpm to obtain a clear supernatant, effectively separating the suspended catalyst. To 3 mL of this supernatant, 0.5 mL of a 1% o-tolidine solution (prepared in 0.1 M HCl) was added. After a two-minute incubation period, the mixture was acidified with 3 mL of 1 M HCl, which induced a distinct color change to yellow. This chromogenic shift corresponds to the formation of the protonated derivative from the two-electron oxidation of o-tolidine. The concentration of this yellow species was then determined by measuring its characteristic absorption band at about 350 nm using UV-Visible spectroscopy.

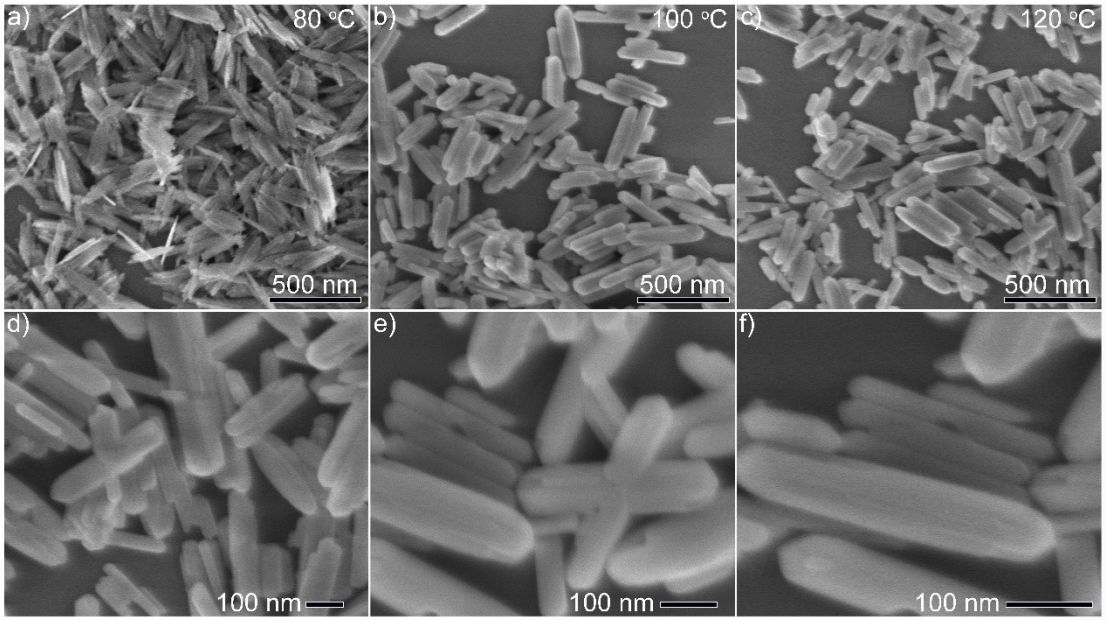

Figure S1 Scanning electron microscopy (SEM) analysis of β-FeOOH catalyst synthesized at different temperatures: a) 80 °C, b) 100 °C, and c) 120 °C, along with high magnification c), d), and e), respectively.

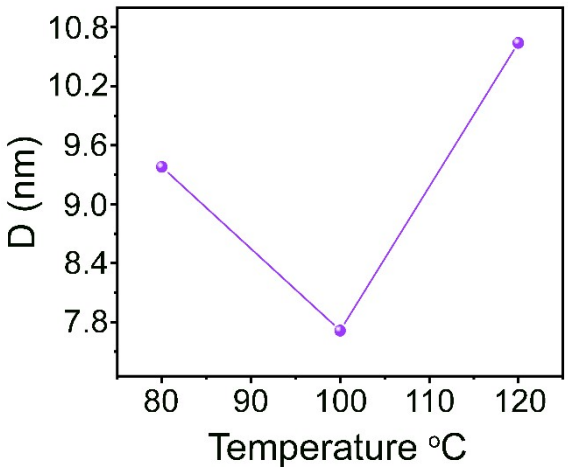

Figure S2 Crystallite size of β-FeOOH nanorods synthesized at temperature 80, 100, and 120 °C, respectively.

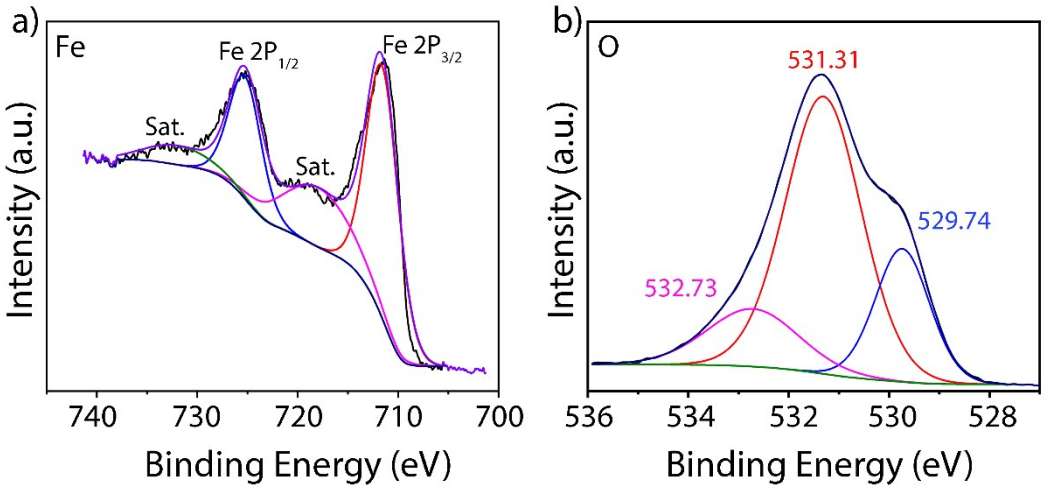

Figure S3 a) Fe 2p XPS analysis of β-FeOOH and b) O 1s of the FeOOH-100 catalyst.

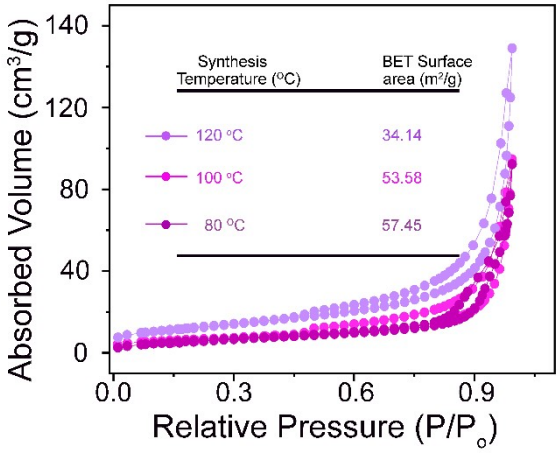

Fig. S4 N_2 absorption/desorption isotherm curves of β-FeOOH nanorods synthesized at different temperatures: a) 80 °C, b) 100 °C, and c) 120 °C, along with BET surface area, respectively.

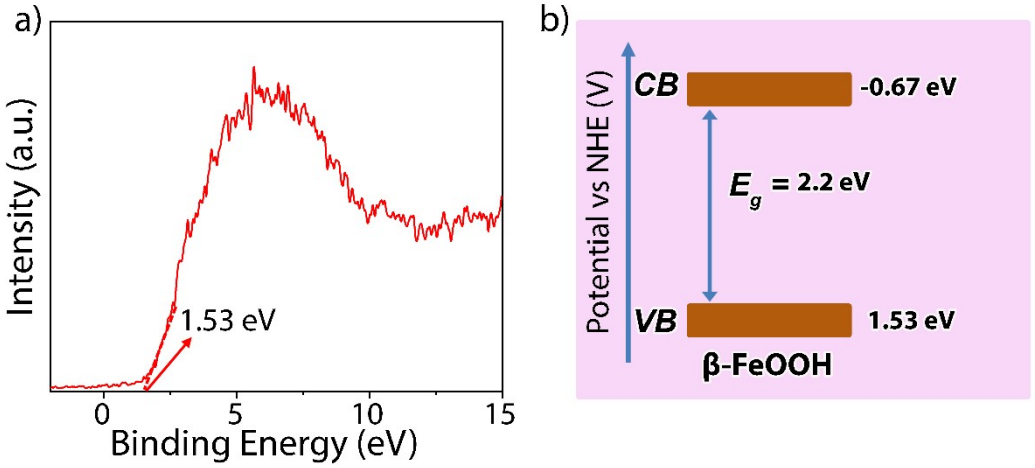

Figure S5 X-ray photoelectron spectroscopy valence band (XPS-VB) and b) energy band structure of the optimized β-FeOOH catalyst.

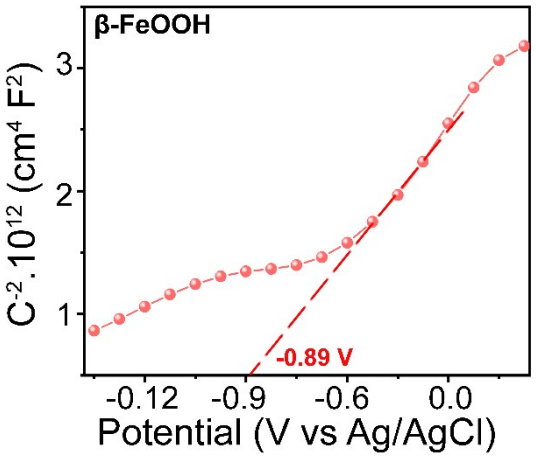

Figure S6. Mott-Schottky analysis of β-FeOOH catalyst.

The detailed calculation of the Band Position

$E = E_{pH} = 0 - 0.059 * pH, (NHE, pH = 7)$.....(1)

$E = E_{Ag/AgCl} - E^{\theta}_{\overline{Ag/AgCl}} + 0.059 * pH, (NHE, pH = 7)$.....(2)

Where $E^{\theta}_{\overline{Ag/AgCl}}$ (pH = 7) is 0.197 V

$\beta - FeOOH,\ E_{CB} = -0.89 - 0.197 + 0.059 * 7 = -0.67$

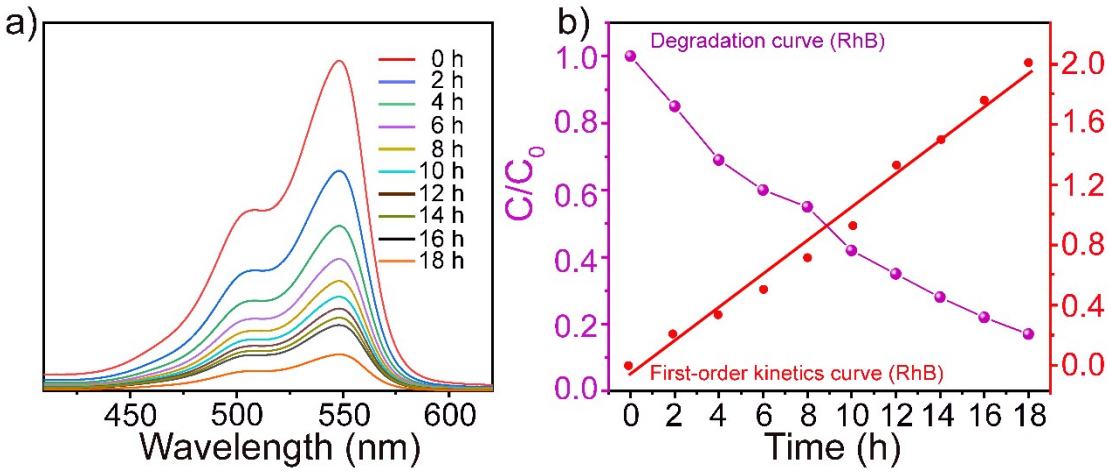

Figure S7 a) UV-vis degradation absorbance analysis vs time b) degradation efficiency curve and ln(C/C_0) vs reaction time of the optimized β-FeOOH catalyst.

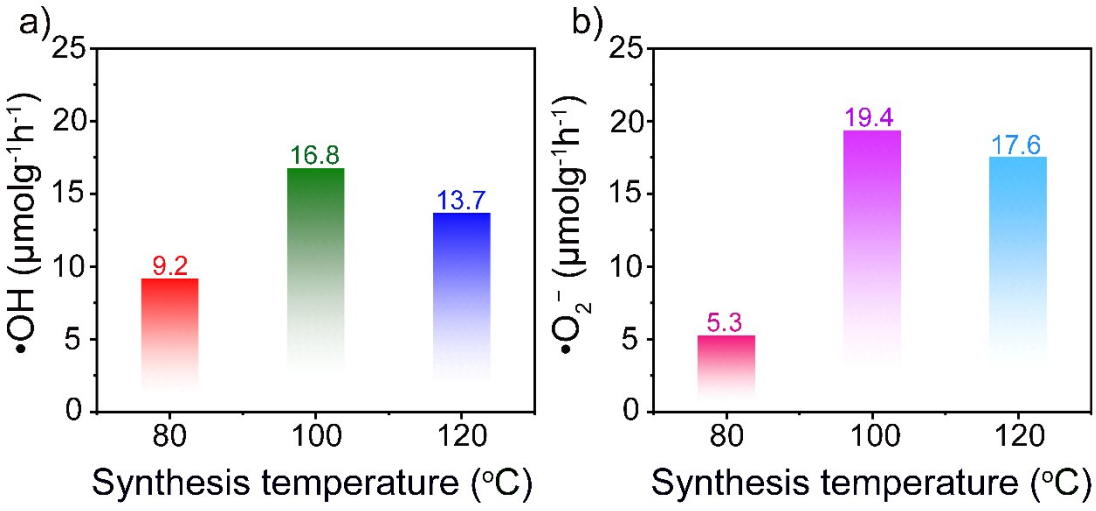

Figure S8 a), b) Represents the yield of •OH radical analysis, and b) the yield of •O2⁻ radical detection of synthesized catalyst at different at temperature to elucidate the reaction process.

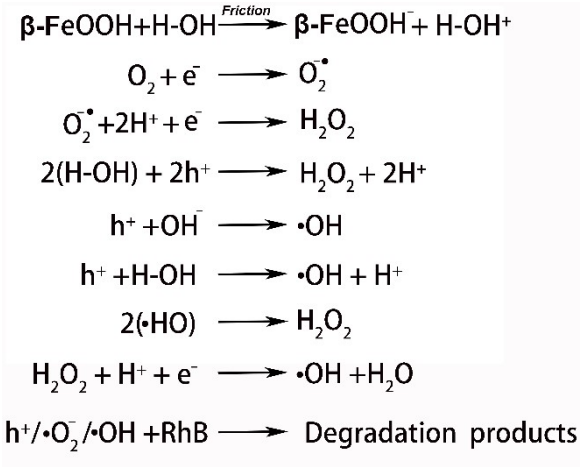

Figure S9 Mechanism involved in the RhB dye degradation process.

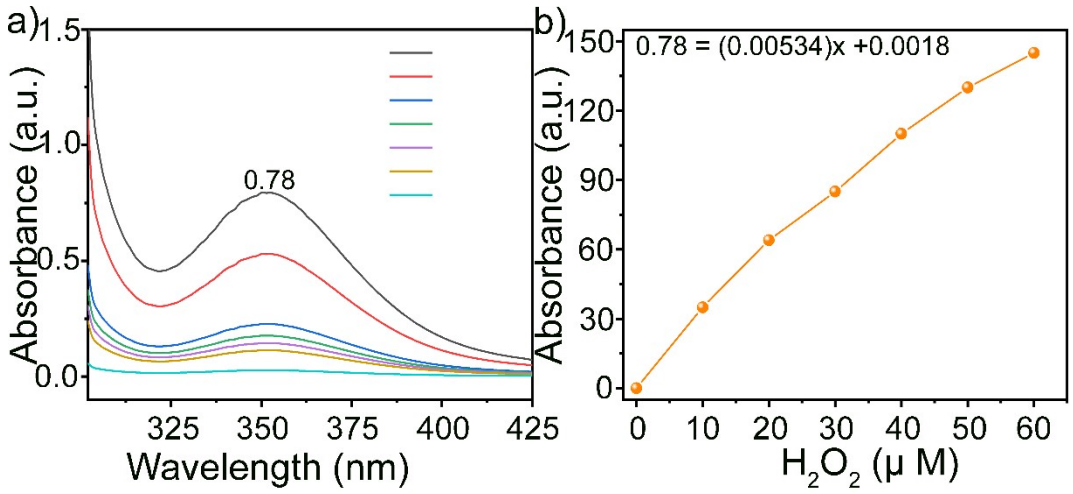

Figure S10 a) UV-vis absorption spectra and iodimetry identified H_2O_2 production in the tribocatalytic process with the optimized β-FeOOH catalyst, and H_2O_2 yield was measured over time.

Table S1: Comparisons analysis based on tribocatalytic of various pollutants degradation.

Catalysts used	Dosage/Dye used	RPM	Degradation (%)	Ref.
β-FeOOH (nanorods)	5 mgL^{-1}/RhB	800	97	This work
$CaCu_3Ti_4O_{12}$	10 mg mL^{-1} (RhB)	700	60	[1]
ZnO and La/ZnO	10 mg L^{-1}(RhB)	500	92	[2]
$BaTiO_3$	16.67 mg mL^{-1} (RhB)	700	84	[3]
Fe-doped Zno	1 mg mL^{-1} (RhB)	800	76	[4]
FeOOH nanorods	5 mg mL^{-1} (RhB)	700	96	[5]

References:

[1] A. Gaur, A. Kumar Moharana, C. Porwal, V. Singh Chauhan, R. Vaish, Degradation of organic dyes by utilizing $CaCu_3Ti_4O_{12}$ (CCTO) nanoparticles via tribocatalysis process, Journal of Industrial and Engineering Chemistry 129 (2024) 341–351. https://doi.org/10.1016/j.jiec.2023.08.048.

[2] D. Ivanova, B. Stefanov, N. Kaneva, A Highly Efficient Tribocatalysis of La/ZnO Powders for Degradation of Rhodamine B, Catalysts 14 (2024) 527. https://doi.org/10.3390/catal14080527.

[3] A. Gaur, C. Porwal, V.S. Chauhan, R. Vaish, Tribocatalytic investigation of $BaTiO_3$ for dye removal from water, Journal of Materials Science: Materials in Electronics 34 (2023) 2154. https://doi.org/10.1007/s10854-023-11511-6.

[4] J. Hu, W. Ma, Y. Pan, Z. Cheng, S. Yu, J. Gao, Z. Zhang, C. Wan, C. Qiu, Insights on the mechanism of Fe doped ZnO for tightly-bound extracellular polymeric substances tribo-catalytic degradation: The role of hydration layers at the interface, Chemosphere 276 (2021) 130170. https://doi.org/10.1016/j.chemosphere.2021.130170.

[5] S. Sun, X. Sui, H. Yu, Y. Zheng, X. Zhu, X. Wu, Y. Li, Q. Lin, Y. Zhang, W. Ye, Y. Liang, High Tribocatalytic Performance of FeOOH Nanorods for Degrading Organic Dyes and Antibiotics, Small Methods 8 (2024). https://doi.org/10.1002/smtd.202301784.