

Supporting Information

Light-Induced Degradation of Organic Pollutants under High Salinity Conditions using Titanium Dioxide / Ferrocene Polymer Nanocomposites as Photocatalyst and H₂O₂ Activator Simultaneously

Jingyu Zhang^{a, b}, Yan Wang^{a, b}, Bin Peng^{a, b}, Shaobin Wen^{a, b}, Qiang Zhang^{a, b, *}

^a Key Laboratory of New Membrane Materials, Ministry of Industry and Information Technology, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

^b Institute of Polymer Ecomaterials, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

* Corresponding author: zhangqiang@njust.edu.cn

Experimental

Materials

Poly (ethylene glycol) methyl ether acrylate ($M_n=480$, PEGA₄₈₀) Azobisisobutyronitrile (AIBN), *N, N*-dimethylformamide (DMF, 99%), Rhodamine B (RhB), Tert-butanol (TBA), bisphenol A (BPA, 99%), bisphenol S (BPS, 99%), tetracyclines (TC, 99%), Titanium dioxide (anatase 99.8% metals basis, average particle size: 25 nm), sodium chloride (NaCl), and sodium nitrate (NaNO₃) were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). Deionized (DI) water used in all experiments was obtained from a Purifier ultrapure water system. *N*-3,4-dihydroxybenzenethyl methacrylamide (DMA) and ferrocenylmethyl methacrylate (FMMA) were homemade [36, 37].

Characterization

The Transmission Electron Microscope (TEM, JEM-3200FS). The Field emission scanning electron microscope (FESEM, S-4800, Hitachi Limited, Japan) was used to illustrate TiO₂@Fc' surface morphologies, and combined with the energy-dispersive X-ray spectroscopy (EDX) component analysis. The functional groups present and thermal stability of TiO₂@Fc were studied by transform infrared (FTIR, Nicolet iS5) and thermogravimetric analyzer (TGA, TGA5500) respectively. The types of ROSs were tested by Electron paramagnetic resonance (EPR, BRUKE EMXPLUS). The light source for simulating light is a 300 W Xe lamp (CEL-HXF 300, Beijing China Education Au-light). Explored intermediates in the degradation were processed by liquid chromatography-mass spectrometry (LC-MS). Total organic carbon (TOC) analysis was applied to test the mineralization degree of RhB during photo Fenton-like reaction. The optical and optoelectronic properties of TiO₂@Fc were characterized by UV-visible diffuse reflection spectrum (Shimadzu UV 3600) and photocurrent response (AH022-125).

Preparation of ferrocene-containing polymer and TiO₂@Fc hybrid nanocomposites

PEGA₄₈₀ (1.92 g), FMMA (1.2 g), DMA (80 mg), and AIBN (26 mg) were added to DMF (40 mL) and agitated for 24 hours at 70°C under the nitrogen atmosphere. Then TiO₂ (4.8 g) was added to the reaction tube and stirred at ambient temperature for 24 hours. After the reaction, the TiO₂@Fc nanocomposites were separated from DMF by centrifugation and purified *via* elution with methanol and water. Finally, the TiO₂@Fc was dried in a vacuum oven at 40 °C (4.5 g), and the yield was 57%.

Investigation of optimal photoreaction conditions

Different amounts of H₂O₂ and TiO₂@Fc were used to investigate the optimal conditions for photo Fenton-like reaction under visible light or simulated sunlight separately. In a typical TiO₂@Fc / H₂O₂ system, 50 mg TiO₂@Fc and 40 μL H₂O₂ were added to a 50 mL RhB solution (20 mg/L). The mixture was stirred at 380 rpm under light separately at room temperature and then every 5 min samples were withdrawn and added 50 μL methanol then filtered through a 0.45 μm filter. The initial absorbance (A₀) of RhB solution at 564 nm was tested *via* UV/Vis spectrophotometer (UV-2600, Shimadzu). All samples in optimal experiments were prepared in triplicate. After the reaction, the absorbance of the filtered solution (A_t) was tested. The formula for the removal ratio is defined by Equation (1):

$$\text{Removal ratio} = \left(1 - \frac{A_t}{A_0}\right) \times 100\% \quad (1)$$

In a typical photocatalytic oxidation reaction, 50 mg TiO₂@Fc were added to a 50 mL RhB solution (20 mg/L), and every 10 min samples were withdrawn. The other conditions were followed in the typical TiO₂@Fc / H₂O₂ system. All samples in the photocatalytic oxidation reaction were prepared in triplicate.

Quenching experiments

To reveal the mechanism involved in the photo-Fenton degradation of RhB, two sets of quenching experiments were conducted to determine the radical species ($\cdot\text{OH}$, and $^1\text{O}_2$) by adding TBA (15 mmol/L), and NaN_3 (15 mmol/L) as obligate scavengers, respectively. N_2 was injected into the solution to test the effect of dissolved oxygen in water. All samples in catalytic degradation experiments were prepared in triplicate. In EPR analysis, dimethyl pyridine N-oxide (DMPO, 50 mmol/L) was used as a trapping agent for $\cdot\text{O}_2^-$ and $\cdot\text{OH}$, and 2, 2, 6, 6-tetramethyl-4-piperidinol (TEMP, 50 mmol/L) was used as a trapping agent for $^1\text{O}_2$.

Effect of high salinity conditions on photo Fenton reaction

NaCl (500 mmol/L) and NaNO₃ (500 mmol/L) were added to test the degradation of RhB in high salinity wastewater under visible light separately. The other conditions were followed in section 2.4. All samples in catalytic degradation experiments were prepared in triplicate.

Reusability of TiO₂@Fc

For reusability tests, the TiO₂@Fc were recovered by centrifugation and washed with methanol and water after the reaction. The other conditions were followed in section 2.4. All samples in catalytic degradation experiments were prepared in triplicate.

Photodegradation of different organic pollutants

To demonstrate the versatility of the photo Fenton reaction, the aqueous solution containing different organic pollutants (BPA, BPS, and TC, 20 mg/L) were selected for degradation at pH 3.0 under visible light or simulated sunlight separately. The other conditions were followed in section 2.4. The concentrations of organic pollutants were tested by HPLC. All samples in catalytic degradation experiments were prepared in triplicate.

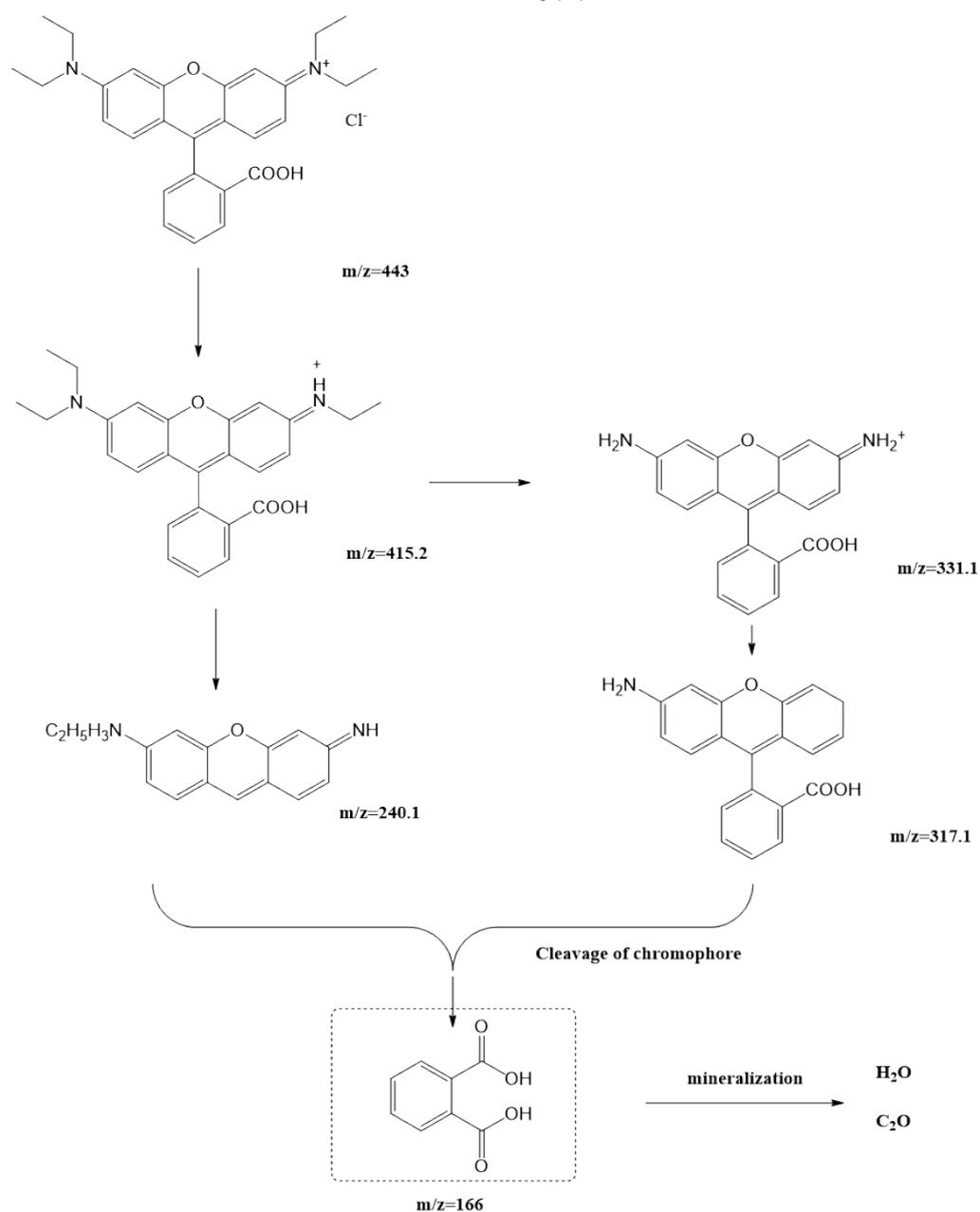
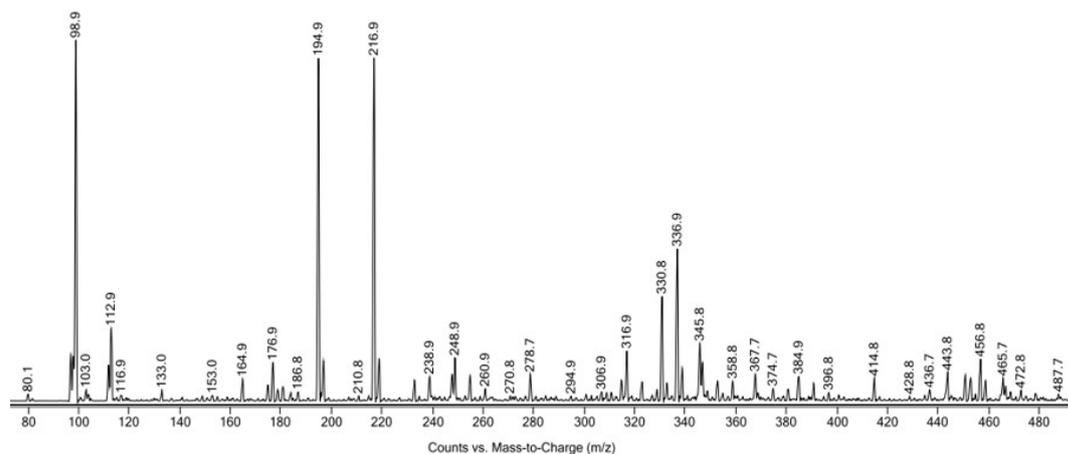


Figure S1 (A) Mass spectrum of RhB (B) Possible photocatalytic degradation pathways of RhB in the photo Fenton-like reaction.

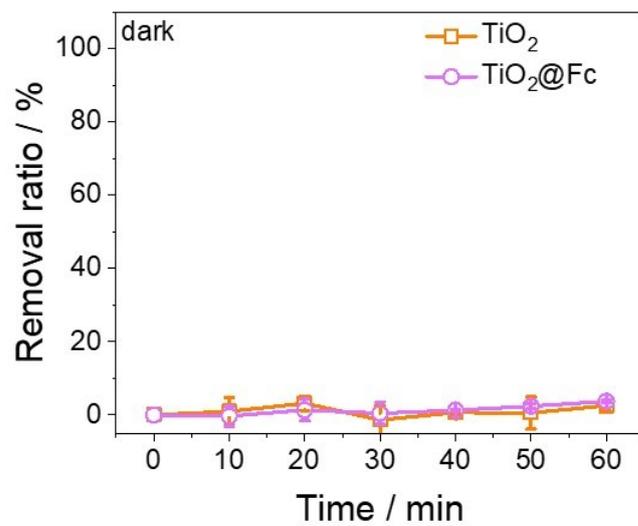


Figure S2. Removal ratio of RhB solution in the presence of $\text{TiO}_2@\text{Fc}$ or TiO_2 in dark.

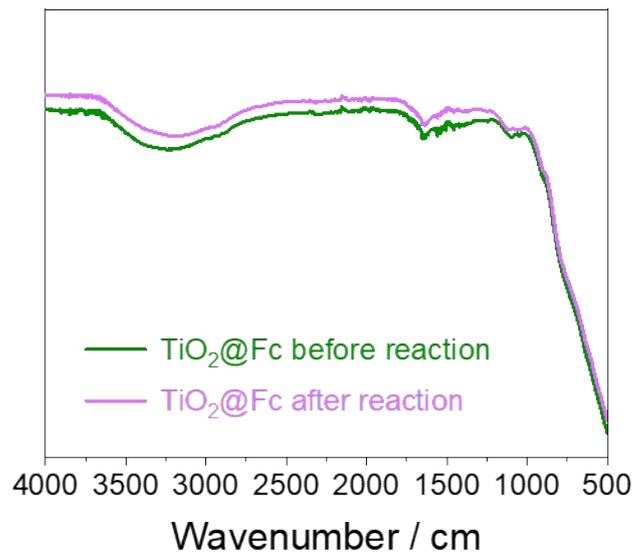


Figure S3. FTIR spectra of TiO₂@Fc before and after the reaction.