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Facile synthesis of Fe₃O₄@pyrogallol-formaldehyde resin@Ag core–shell nanomaterials for the catalytic degradation of contaminants

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Noble metal nanoparticles (NPs) show excellent performance in catalysis, but their strong aggregation effect can lead to a decrease in or even disappearance of their catalytic activity. In this study, Fe₃O₄@pyrogallol-formaldehyde resin@Ag (Fe₃O₄@PGFR@Ag) nanomaterials were synthesized using Fe₃O₄ as a magnetic core and pyrogallol-formaldehyde resin (PGFR) as a shell layer. The presence of Fe₃O₄ ensured rapid material recovery. At the same time, the phenolic hydroxyl group in PGFR enabled the *in situ* reduction of Ag⁺ to form embedded Ag NPs, effectively avoiding the aggregation and shedding of Ag NPs. Cetyltrimethylammonium bromide (CTAB) was used to modify the surface charge of the catalyst. Results showed that negatively charged Fe₃O₄@PGFR@Ag exhibited high catalytic activity, with a 90% higher catalytic rate constant for cationic dye rhodamine B (RhB) compared with Fe₃O₄@PGFR@Ag-CTAB. Positively charged Fe₃O₄@PGFR@Ag-CTAB showed high catalytic activity, with a 124% higher catalytic rate constant for the anionic dye methyl orange (MO) compared with Fe₃O₄@PGFR@Ag. Therefore, the matching of the charges of the catalyst and contaminants, which facilitates the adsorption of the pollutants around the catalyst, has a significant impact on the catalytic performance and should be considered in the process of pollutant treatment.

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1. Introduction

The rapid development of modern industries has brought great convenience to humanity, but it has resulted in serious water pollution.^{1–3} Many organic dyes exhibiting persistent biotoxicity are difficult to degrade and enter the natural water circulation system *via* industrial wastewater, posing a significant threat to human survival and the sustainable and healthy development of the natural environment.^{4–7} Anionic dyes such as methyl orange (MO), which is widely used in leather and wool production; rhodamine B (RhB), used in the cosmetics industry; and tetracycline (TC), used in the medical sector, can pose a serious threat to the health of the natural environment and the survival of flora and fauna if improperly treated.^{8,9} Therefore, organic dye removal and rapid decolorization have become important research topics. Noble metal nanoparticles have been identified as an effective means to achieve this goal and have attracted much attention in the past few decades.^{10–13}

According to reports, noble metal nanoparticles have good catalytic selectivity for organic pollutants and have attracted extensive attention from researchers in the past few decades.^{14–16} Ag nanoparticles (NPs) can quickly realize electron transfer in a catalytic system, accelerating the catalytic

hydrogenation process on the surface of organic pollutants, ultimately leading to the decolorization of organic pollutants such as RhB and MO.^{17–20} However, the strong aggregation tendency of Ag nanoparticles makes them easily agglomerate, resulting in a decrease in or even disappearance of their catalytic activity.^{21–28} Moreover, individual nanoparticles are difficult to separate from the catalytic system, making it impossible to achieve controlled recycling of the catalytic material. Therefore, magnetic core–shell materials that can be quickly recycled and stably loaded onto noble metal nanoparticles have attracted researchers' attention.^{29–35}

In this study, we designed Fe₃O₄@PGFR@Ag nanomaterials, which are composed of magnetic Fe₃O₄ as a core material and pyrogallol-formaldehyde resin (PGFR) as a shell material. The presence of magnetic core materials ensures the rapid recovery of nanoparticles after catalysis. PGFR possesses strong adhesion and easy surface modification properties. During the reduction of AgNO₃, the phenolic hydroxyl groups on the surface of PGFR enable the *in situ* reduction of AgNO₃ without external reducing agents. By contrast, in silicon-based material systems, the reduction of AgNO₃ requires the addition of external reducing agents, such as hydrazine hydrate. Fe₃O₄@PGFR@Ag exhibits excellent catalytic activity for the cationic dye RhB. Therefore, nanomaterials whose surface charges are switched using CTAB exhibit efficient catalytic activity toward anionic dyes.

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2. Experimental section

2.1 Materials and chemicals

Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), trisodium citrate dihydrate, ethylene glycol, anhydrous sodium acetate, pyrogallol, a formaldehyde solution (37–40%), an ammonium solution (25–28%), silver nitrate, sodium borohydride (NaBH_4), cetyltrimethylammonium bromide, rhodamine B (RhB), tetracycline (TC), and methyl orange (MO) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

2.2 Synthesis of Fe_3O_4

The synthesis of Fe_3O_4 nanoparticles was performed using the following procedure.³⁶ Briefly, 1.08 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.46 g of trisodium citrate were added to 40 mL of ethylene glycol to form a dispersed solution by stirring at room temperature. Then, 2.4 g of anhydrous sodium acetate was added to the above solution. The above solution was stirred for 30 min and then transferred to a closed polytetrafluoroethylene reactor for 12 h at 200 °C. Then, the reactor was cooled to room temperature. The black precipitate was collected using a magnetic block and repeatedly washed with deionized water and ethanol. Then, the obtained black powder was dried under vacuum at 60 °C for 6 h.

2.3 Synthesis of Fe_3O_4 @PGFR

The prepared Fe_3O_4 particles (0.08 g) and pyrogallol (0.1637 g) were uniformly dispersed in 200 mL of a deionized water solution containing 142 μL of ammonia and stirred well. Then, a formaldehyde solution (222 μL) was added to the solution, dispersed evenly by stirring for 30 minutes, heated to 80 °C, and maintained for 30 minutes. After the completion of the reaction, Fe_3O_4 @PGFR was thoroughly washed with deionized water and ethanol, separated using a magnet, and dried under vacuum for 6 h.

2.4 Synthesis of Fe_3O_4 @PGFR@Ag and Fe_3O_4 @PGFR@Ag-CTAB

The preparation procedure of the Fe_3O_4 @PGFR@Ag nanomaterial is as follows. The prepared Fe_3O_4 @PGFR (25 mg) was

dispersed in 50 mL of an aqueous silver nitrate (2 mM) solution and stirred at room temperature in a dark environment for 2 hours. Fe_3O_4 @PGFR@Ag was washed several times with deionized water and ethanol, magnetically separated, and dried under vacuum for 6 hours. The charge conversion of Fe_3O_4 @PGFR@Ag NPs was achieved by immersing Fe_3O_4 @PGFR@Ag in a CTAB solution for 24 hours (named as Fe_3O_4 @PGFR@Ag-CTAB). The synthesis route is shown in Fig. 1.

2.5 Characterization

The transmission electron microscopy (TEM) images were obtained using JEM-2100F. Scanning electron microscopy (SEM) images were obtained using a Zeiss Merlin compact field-emission instrument at an accelerating voltage of 20 kV. The Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Equinox 55 spectrometer in the transmission mode in the scan range from 4000 to 500 cm^{-1} . The UV-vis absorption spectra were recorded on a UV-3600 spectrophotometer (Shimadzu, Japan). The zeta potentials were measured using a NanoBrook 90Plus Zeta nanograin-sized analyzer (Brookhaven, USA). The magnetic characteristics of the samples were studied using a vibrating sample magnetometer (VSM) (HH-20, China) at an applied field between -1500 and 1500 Oe at room temperature. The X-ray diffraction (XRD) patterns were measured using an XRD-6000 X-ray diffractometer (Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) results were recorded on an Axis Ultra DLD system using Al $K\alpha$ radiation.

2.6 Catalytic performance test

Initially, an aqueous solution of Fe_3O_4 @PGFR@Ag was prepared at a concentration of 0.25 mg mL^{-1} . Subsequently, the aqueous Fe_3O_4 @PGFR@Ag solution (200 μL) was added to a mixed solution containing 2 mL of RhB (10 mg mL^{-1}) and 1 mL of a freshly prepared sodium borohydride (0.5 M) solution. The concentration change of the solution was monitored using a UV-vis spectrometer. The catalytic activity of Fe_3O_4 @PGFR@Ag for RhB was evaluated using a quasi-level kinetic equation. The same procedure was followed for methyl orange

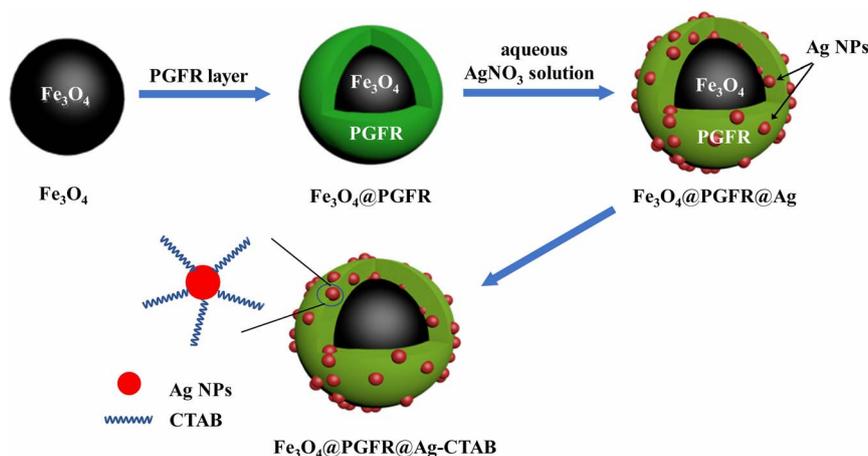


Fig. 1 Synthesis route for Fe_3O_4 @PGFR@Ag-CTAB core-shell nanomaterials.



and tetracycline. To assess the catalytic cyclability of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$, an aqueous solution of the contaminant (1 mg mL^{-1} , $20 \mu\text{L}$) was added to the reaction system for the next catalytic cycle. The catalytic performance of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$ NPs was evaluated using the same method.

3. Results and discussion

3.1 Characterization of $\text{Fe}_3\text{O}_4\text{-PGFR}$, $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$, and $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$

The SEM and TEM images of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{-PGFR}$, and $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$ are presented in Fig. 2. As shown in Fig. 2a, Fe_3O_4 NPs exhibited a regular and uniform spherical structure with a relatively rough surface. After coating Fe_3O_4 NPs with PGFR (Fig. 2c), $\text{Fe}_3\text{O}_4\text{-PGFR}$ core-shell nanoparticles were formed, with PGFR uniformly coating the surface of Fe_3O_4 NPs. The surface of $\text{Fe}_3\text{O}_4\text{-PGFR}$ became smooth, and the thickness of the PGFR layer was approximately 30 nm (Fig. 2d). The TEM image of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$ (Fig. 2f) revealed that Ag NPs were successfully captured and immobilized within the shell of PGFR. This suggests that the phenolic hydroxyl groups in the PGFR layer can form coordination complexes with silver ions and reduce them to silver nanoparticles, which then grow on the PGFR shell.

The TEM images of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$ prepared with different silver nitrate contents and the Ag^0 particle size distributions are shown in Fig. 3. The results indicate that the particle size of Ag NPs increased with an increase in the AgNO_3 dosage. With an increase in the dosage of AgNO_3 , a higher amount of Ag^+ diffused into the shell layer of PGFR, where it was captured and anchored for reduction deposition. It is also owing to its adhesion properties that $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$ aggregation occurs. The overall size distribution of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$ is shown in Fig. 4.

The X-ray diffraction (XRD) patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$, and $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$ nanomaterials are shown in Fig. 5. The seven peaks at 18.3° , 30.1° , 35.8° , 43.1° , 54.4° , 57.0° , and 62.6° corresponded to the (1 1 1), (2 2 0), (3 1 1), (4 4 0), (4 2 2), (5 1 1), and (4 4 0) planes of Fe_3O_4 , respectively (JCPDS card no. 19-0629). The XRD pattern of the

$\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$ nanohybrid material also confirmed the presence of Ag NPs with four new peaks at 38.1° , 44.3° , 64.4° , and 77.5° , corresponding to the (111), (200), (220), and (311) planes of Ag NPs, respectively (JCPDS card no. 04-0783). The XRD patterns of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$ and $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$ did not differ significantly. This indicates that surface modification by CTAB does not affect the crystalline shape and the presence of Ag NPs. Ag NPs can still maintain their good catalytic activity. The HRTEM images of Ag NPs are shown in Fig. 5b. According to Image J calculations, the lattice spacing of Ag NPs was 0.238 nm (Fig. 5c), corresponding to the (111) crystal plane of the face-centered cubic (fcc) structure. The diffraction spots (Fig. 5c) are the FFT of the areas marked by the red box in Fig. 5b.

FT-IR spectroscopy was employed to investigate the chemical structure of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$ core-shell materials. The spectra of the samples are presented in Fig. 6. The peak observed at 580 cm^{-1} corresponded to the stretching vibration of the Fe-O bond in pure Fe_3O_4 NPs (Fig. 6a). The two peaks observed at 1305 cm^{-1} and 1112 cm^{-1} corresponded to the stretching vibrations of the C-O bond and the C-O-C vibrational mode, respectively, indicating the presence of the PGFR coating on Fe_3O_4 NPs. As shown in Fig. 6c and d, $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$ exhibited four additional distinct peaks at 910 cm^{-1} , 957 cm^{-1} , 2845 cm^{-1} , and 2913 cm^{-1} compared to $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$. The peaks at 910 cm^{-1} and 957 cm^{-1} were attributed to the in-plane C-H bending vibrations, while the peak at 2845 cm^{-1} corresponded to the stretching vibration of $-\text{CH}_2$. The peak at 2913 cm^{-1} was assigned to the C-H stretching vibration of the saturated carbon of the CTAB end group ($-\text{CH}_3$). These results confirm the successful preparation of the $\text{Fe}_3\text{O}_4\text{-PGFR@Ag-CTAB}$ nanohybrid materials.

To further demonstrate the presence of silver as a monomer in the hybrid material, the X-ray photoelectron spectroscopy (XPS) spectra of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$ nanomaterials were recorded and are presented in Fig. 7. The full-scan XPS spectra of the samples showed the presence of the O 1s orbital, C 1s orbital, and Ag 3d orbital. The high-resolution XPS spectrum of Ag 3d in Fig. 7b revealed that the 3/2 and 5/2 peaks of the Ag 3d orbital were located at 374.2 eV and 368.3 eV, respectively. Previous

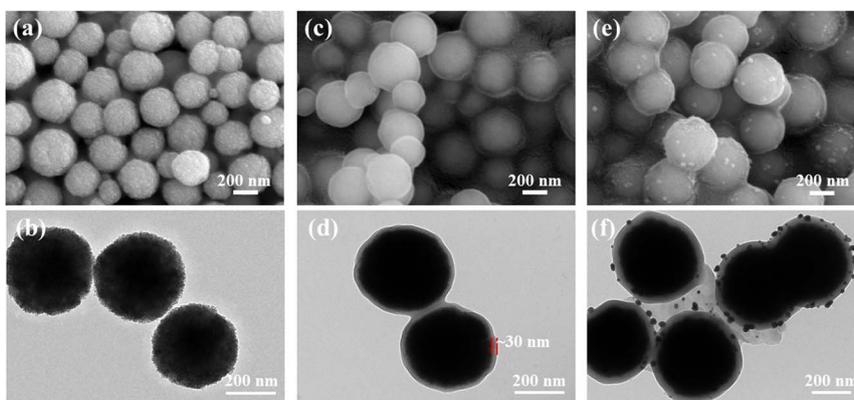


Fig. 2 SEM and TEM images. (a) SEM image of Fe_3O_4 , (b) TEM image of Fe_3O_4 , (c) SEM image of $\text{Fe}_3\text{O}_4\text{-PGFR}$, (d) TEM image of $\text{Fe}_3\text{O}_4\text{-PGFR}$, (e) SEM image of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$, and (f) TEM image of $\text{Fe}_3\text{O}_4\text{-PGFR@Ag}$.

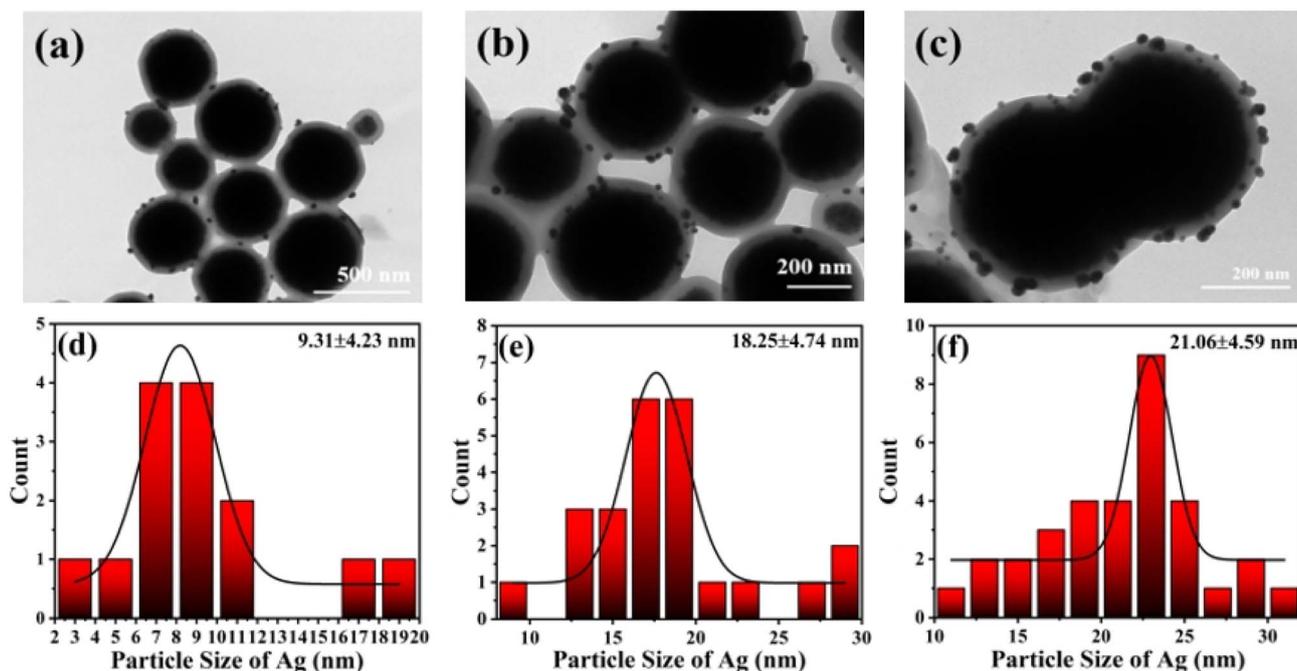


Fig. 3 TEM images of (a) Fe_3O_4 @PGFR@Ag-0.5 mM, (b) Fe_3O_4 @PGFR@Ag-1 mM, and (c) Fe_3O_4 @PGFR@Ag-2 mM. (d) Particle size distribution of Ag NPs-0.5 mM, (e) particle size distribution of Ag NPs-1 mM, and (f) particle size distribution of Ag NPs-2 mM.

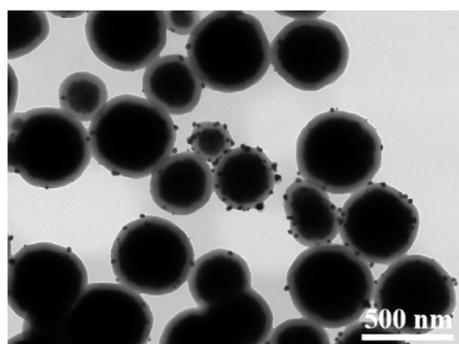


Fig. 4 Overall size distribution of Fe_3O_4 @PGFR@Ag-CTAB.

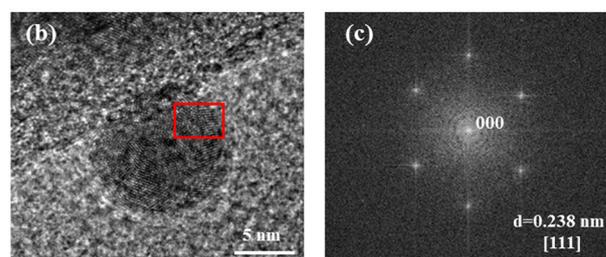
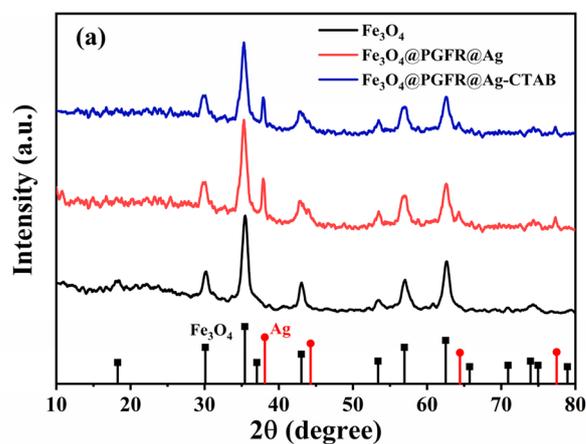


Fig. 5 (a) XRD patterns of Fe_3O_4 , Fe_3O_4 @PGFR@Ag, and Fe_3O_4 @PGFR@Ag-CTAB. (b) HRTEM image of Fe_3O_4 @PGFR@Ag. (c) FFT of Fe_3O_4 @PGFR@Ag.

reports have shown that the single silver peak corresponds to a binding energy of around 370 eV, which is typical for metallic silver. This confirms that the metallic silver presented in the Fe_3O_4 @PGFR@Ag nanohybrid material is the active material required for subsequent catalysis. XPS further confirmed that silver in the hybrid material existed as a monomer. Fig. 7c shows three peaks based on the C 1s fitted deconvolution, with C 1s binding energies at 284.2 eV, 285.5 eV, and 288.0 eV, corresponding to the C-C bond, C-O bond, and C=O double bond of PGFR, respectively. The TEM image (Fig. 2f) demonstrated the successful encapsulation of Fe_3O_4 by the PGFR layer. Ag NPs were reduced by capturing Ag^+ using the phenolic hydroxyl group, which facilitated the growth of Ag NPs on the PGFR shell layer.

The thermogravimetric (TG) curves of Fe_3O_4 , Fe_3O_4 @PGFR, and Fe_3O_4 @PGFR@Ag nanomaterials are presented in Fig. 8a.

Catalytic reactions often occur in complex environments, such as high temperatures and heat, and the thermal stability of materials can have a significant impact on their catalytic



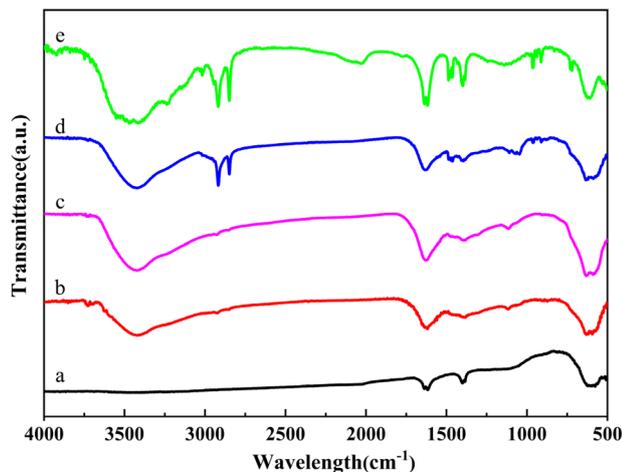


Fig. 6 FT-IR spectra of (a) Fe₃O₄, (b) Fe₃O₄@PGFR, (c) Fe₃O₄@PGFR@Ag, (d) Fe₃O₄@PGFR@Ag-CTAB, and (e) CTAB.

performance. As shown in Fig. 8a, when the temperature was below 160 °C, the weight loss of Fe₃O₄ nanoparticles was due to the evaporation of residual water and organic solvents in the material during the heating process. In the temperature range

from 200 °C to 270 °C, the weight loss of the sample was attributed to thermal decomposition and carbonization caused by the thermal degradation and carbonization of trisodium citric acid, which served as a stabilizer for iron tetroxide. For Fe₃O₄@PGFR, the approximately 43.5 wt% mass loss was mainly due to the carbonization of the PGFR shell when the temperature increased to around 700 °C. The rapid weight loss of Fe₃O₄@PGFR at approximately 700 °C was attributed to the collapse of its core-shell structure.

The mass loss of Fe₃O₄@PGFR@Ag was approximately 39.7 wt%, which is lower than that of Fe₃O₄@PGFR nanoparticles. As shown in Fig. 8a, Fe₃O₄@PGFR and Fe₃O₄@PGFR@Ag exhibited similar weight loss stages from 200 °C to 800 °C, but they differed significantly from pure Fe₃O₄. This indicates that the PGFR shell layer is successfully encapsulated around Fe₃O₄ and Ag NPs are grown *in situ* on the PGFR shell layer. The presence of the PGFR layer had a significant effect on the thermal stability of the catalytic materials. The magnetic properties of the samples were characterized by VSM, as shown in Fig. 8b. The saturation magnetization of pure Fe₃O₄ was measured to be 34.5 emu g⁻¹. After coating with PGFR, Fe₃O₄@PGFR exhibited a reduced magnetization of 18.3 emu g⁻¹. Fe₃O₄@PGFR@Ag displayed a slight decrease in magnetization (16.9 emu g⁻¹). This reduction did not significantly impact the

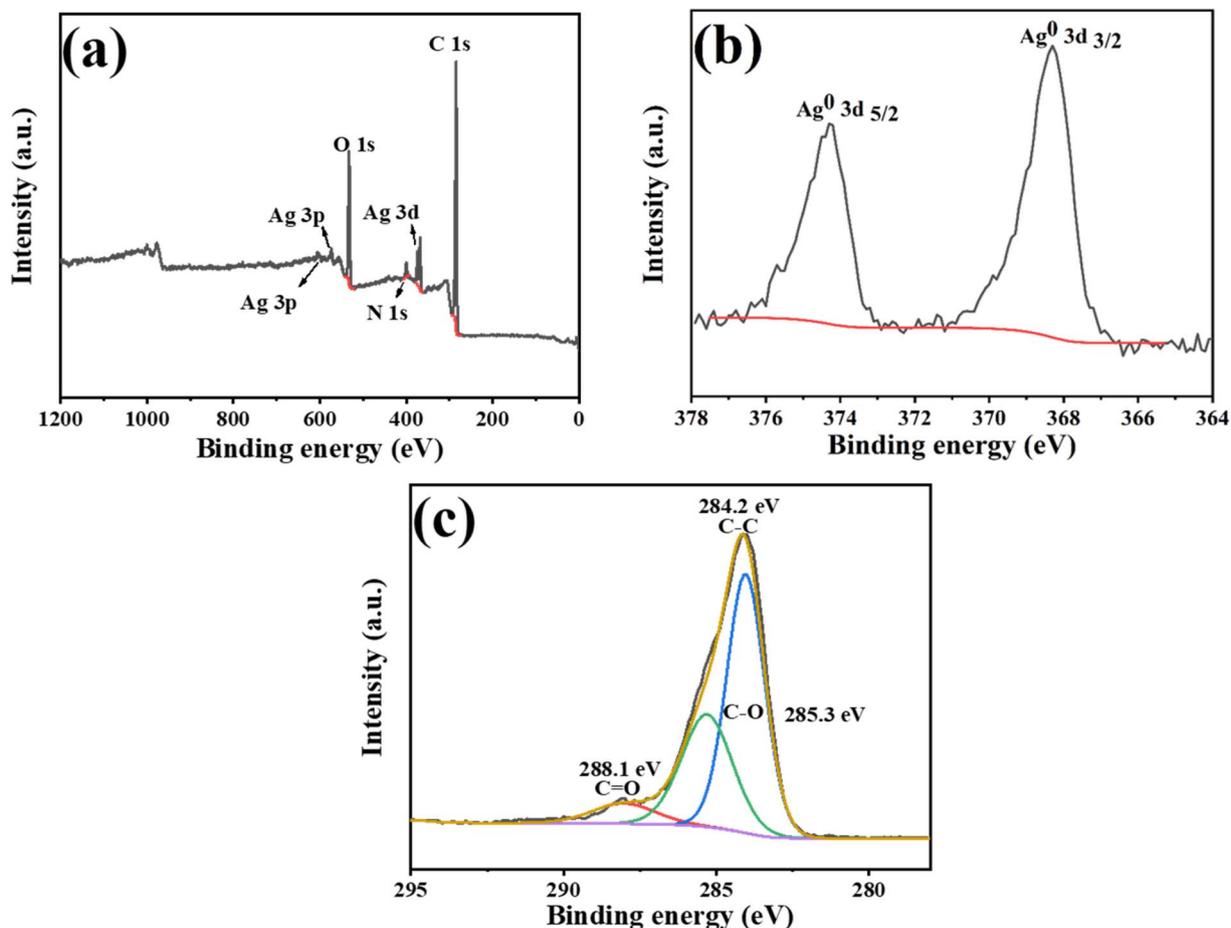


Fig. 7 XPS spectra of Fe₃O₄@PGFR@Ag: (a) full-scan, (b) Ag 3d, and (c) C 1s spectra.

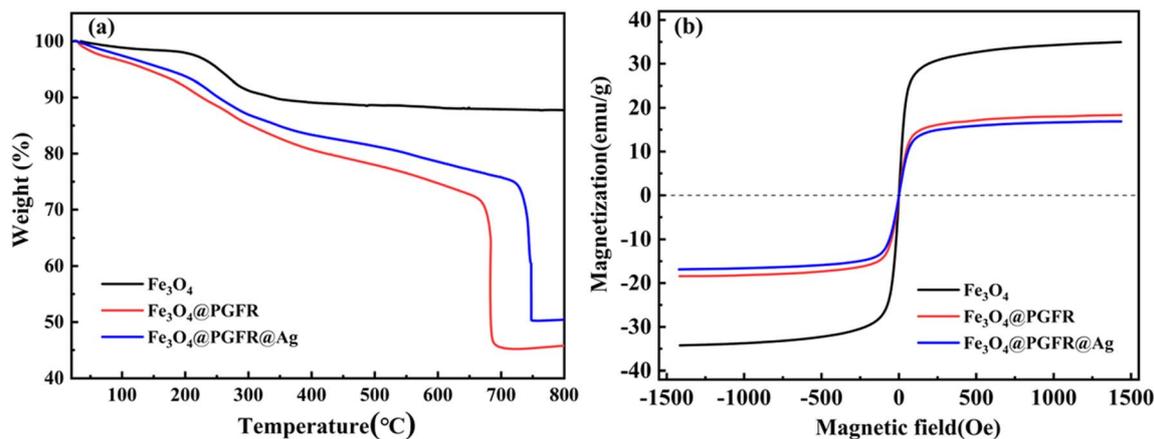


Fig. 8 (a) TG curves of Fe₃O₄, Fe₃O₄@PGFR, and Fe₃O₄@PGFR@Ag. (b) VSM curves of Fe₃O₄, Fe₃O₄@PGFR and Fe₃O₄@PGFR@Ag.

magnetic recovery performance of Fe₃O₄@PGFR@Ag, as evidenced by its efficient separation from the solution using an external magnetic field.

Fig. 9 shows the zeta potentials of Fe₃O₄@PGFR@Ag and Fe₃O₄@PGFR@Ag-CTAB. The zeta potential of Fe₃O₄@PGFR@Ag was approximately -36.3 mV (Fig. 9). Due to the surface electrostatic attraction, a negative surface charge state would exhibit higher catalytic properties for cationic dyes such as RhB. Therefore, changing the surface charge state of the nanomaterial is crucial for preparing nanomaterials with high catalytic performance for anionic dyes such as MO. CTAB, as a cationic surfactant, can combine with metal particles to form noble metal particle-CTAB. This allows the surface charge state of noble metal particles to transition from negative to positive. Fe₃O₄@PGFR@Ag-CTAB nanoparticles with a positive surface charge were obtained by modifying Fe₃O₄@PGFR@Ag with CTAB. The zeta potential of Fe₃O₄@PGFR@Ag-CTAB was approximately 15.1 mV (Fig. 9). The XRD pattern of Fe₃O₄@PGFR@Ag-CTAB did not differ significantly from that of Fe₃O₄@PGFR@Ag (Fig. 5), indicating that modification with CTAB only changed the surface charge state of the materials without

altering the structure of Fe₃O₄@PGFR@Ag-CTAB or the presence state of Ag NPs.

3.2 Catalytic properties of Fe₃O₄@PGFR@Ag and Fe₃O₄@PGFR@Ag-CTAB

Silver nanoparticles have been reported to exhibit excellent catalytic activity and good selectivity towards organic dyes. Therefore, we investigated the catalytic performance of Fe₃O₄@PGFR@Ag and Fe₃O₄@PGFR@Ag-CTAB towards MO, RhB, and TC in the presence of NaBH₄. Fig. 10a shows a schematic diagram of the catalytic process for the three substrate models. In brief, the catalysis of the three substrates, which are enriched on the surface of Ag NPs, is achieved *via* the transfer of free electrons of Ag NPs. The UV-vis spectra of MO catalyzed by Fe₃O₄@PGFR@Ag are presented in Fig. 10b. It can be observed that after the addition of 200 μ L of the Fe₃O₄@PGFR@Ag catalyst into the catalytic system, the intensity of the characteristic peak of MO at 465 nm began to decrease, and the intensity of the characteristic peak decreased with increasing catalytic time. When the catalyst was added for approximately 3 minutes, the peak of MO at 465 nm disappeared completely, indicating that the catalytic reaction was completed and MO had been reduced. The catalytic rate of Fe₃O₄@PGFR@Ag for MO was 1.564 min^{-1} . When 200 μ L of the Fe₃O₄@PGFR@Ag-CTAB catalyst was added to the MO solution, the characteristic peak of MO at 465 nm rapidly decreased and disappeared within approximately 1 minute. The catalytic rate of Fe₃O₄@PGFR@Ag-CTAB for MO was 3.510 min^{-1} . These results demonstrate that positively charged Fe₃O₄@PGFR@Ag-CTAB significantly enhances the catalytic rate for the anionic dye MO. The MO molecule is enriched on the surface of Ag NPs due to electrostatic effects. This facilitates the rapid acceptance of free electrons generated from the hydrolysis of NaBH₄, which is attacked by free electrons, and the N=N bonds break to form N-H bonds.

To further analyze the effect of the surface charge state of the catalytic material on its catalytic performance, we conducted comparative catalytic experiments using the cationic dye RhB. As shown in Fig. 10e, the intensity of the characteristic peak of

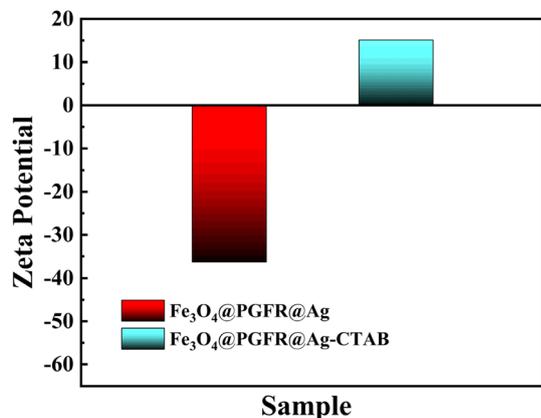


Fig. 9 Zeta potentials of Fe₃O₄@PGFR@Ag and Fe₃O₄@PGFR@Ag-CTAB.



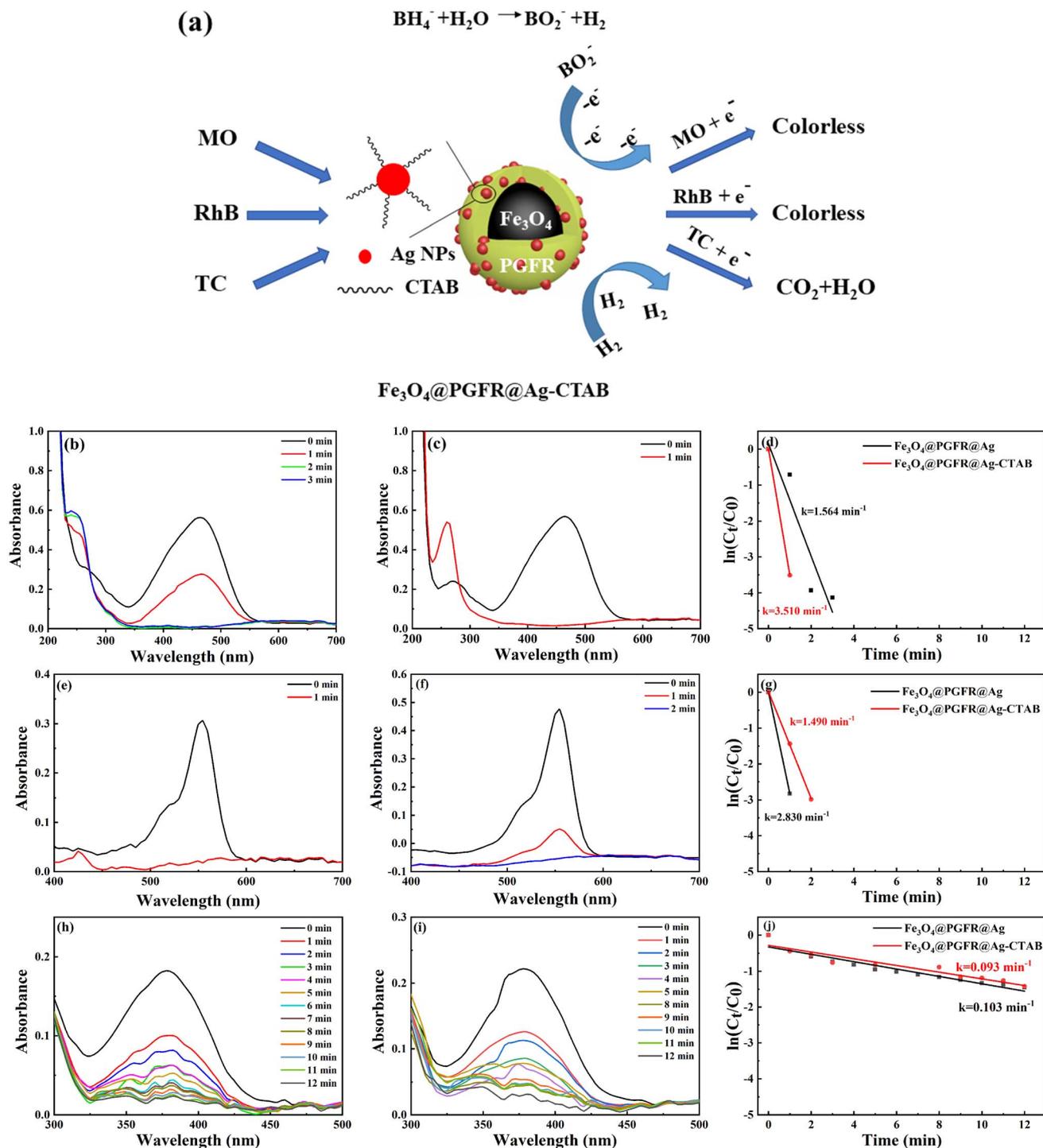


Fig. 10 (a) Schematic of the catalytic process. UV-vis spectra for MO: (b) Fe₃O₄@PGFR@Ag and (c) Fe₃O₄@PGFR@Ag-CTAB. (d) Comparison of first-order rates of reductive degradation. UV-vis spectra for RhB: (e) Fe₃O₄@PGFR@Ag and (f) Fe₃O₄@PGFR@Ag-CTAB. (g) Comparison of first-order rates of reductive degradation. UV-vis spectra for TC: (h) Fe₃O₄@PGFR@Ag and (i) Fe₃O₄@PGFR@Ag-CTAB. (j) Comparison of first-order rates of reductive degradation.

RhB at 550 nm decreased rapidly after the catalyst was added. Due to the electrostatic effect, the cationic dye RhB was more easily enriched on the surface of Fe₃O₄@PGFR@Ag with a negative surface charge. The cationic dye RhB was catalyzed, and new RhB molecules were re-attracted to the surface of Ag

NPs, reaching a kinetic equilibrium. The catalytic rate k was 2.830 min⁻¹, according to the fitting of the first-order kinetic equation. For Fe₃O₄@PGFR@Ag-CTAB (Fig. 10f), the positive surface charge was retarded due to the aggregation of RhB molecules on Ag NPs, which delayed the time required for RhB



Table 1 Catalytic rates of the samples for MO, RhB, and TC

Sample	k for RhB (min^{-1})	k for MO (min^{-1})	k for TC (min^{-1})
$\text{Fe}_3\text{O}_4@PGFR@Ag$	2.830	1.564	0.103
$\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$	1.490	3.510	0.093

Table 2 Comparison of the TC catalytic degradation performance of different catalytic materials

Sample	TC	Catalyst dosage	k (min^{-1})	Ref.
$\text{Fe}_3\text{O}_4/\text{BiVO}_4/\text{CdS}$	10 mg L^{-1}	100 mg	0.023	37
$\text{Fe}_3\text{O}_4/\text{CuO}/\text{C}$	50 mg L^{-1}	300 mg	0.923	38
Bi_2O_3 QDs/g- C_3N_4	10 mg L^{-1}	50 mg	0.014	39
Ag-g- C_3N_4	20 mg L^{-1}	50 mg	0.041	40
AgI/Ag/Cu-BTC	5 mg L^{-1}	80 mg	0.022	5
$\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$	2 mL, 10 mg L^{-1}	0.25 mg mL^{-1} , 200 μL (0.05 mg)	0.103	This work

molecules to reach the Ag NP surface. The catalytic rate constant (k) was calculated to be 1.490 min^{-1} ; notably, this value was lower than that of $\text{Fe}_3\text{O}_4@PGFR@Ag$ ($k = 2.830 \text{ min}^{-1}$). The catalytic rate constants for the three pollutants are presented in Table 1. The surface charge state of the samples had a significant impact on the catalytic performance of the pollutants. In the case of catalysts and contaminants with opposite charges, the contaminants tended to accumulate around the catalyst owing to electrostatic attraction and subsequently undergo further decolorization and degradation by Ag. However, when the charge state of the catalyst and the contaminant was the same, the contaminants were less likely to accumulate around the catalyst owing to electrostatic repulsion, and the catalytic reaction rate constant was significantly reduced.

To evaluate the catalytic performance of $\text{Fe}_3\text{O}_4@PGFR@Ag$ and $\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$, neutral tetracycline (TC) was selected as a test substrate. As shown in Fig. 10h, the intensity of the characteristic peak at 380 nm decreased with the progress of the reaction and disappeared after approximately 12 minutes.

Compared with $\text{Fe}_3\text{O}_4@PGFR@Ag$, the catalytic capacity of $\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$ for TC did not differ significantly. According to the fitting calculation of the first-order kinetic equation (Fig. 10j), the catalytic rate constants of $\text{Fe}_3\text{O}_4@PGFR@Ag$ nanoparticles and $\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$ nanoparticles for TC were 0.103 min^{-1} and 0.093 min^{-1} , respectively (Table 1). These results indicate that switching the material surface charge has little effect on the catalytic performance of neutral TC.

The catalytic properties of various catalytic materials for MO, RhB, and TC are summarized in Tables 2–4, respectively. Compared to the catalysts reported in previous studies, $\text{Fe}_3\text{O}_4@PGFR@Ag$ and $\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$ exhibited superior catalytic performance.

3.3 Stability and recyclability

To assess the stability and recyclability of the catalytic materials, $\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$ was employed to catalyze MO. Six

Table 3 Comparison of the MO catalytic degradation performance of different catalytic materials

Sample	MO	Catalyst dosage	k (min^{-1})	Ref.
$\text{GO}/\text{TiO}_2/\text{Fe}_3\text{O}_4$	50 mL, 10 mg L^{-1}	60 mg	0.022	41
Au-TA	50 mL, 8 mg L^{-1}	50 μL	0.005	42
Ag-TA	50 mL, 8 mg L^{-1}	50 μL	0.59	42
$\text{Fe}_3\text{O}_4@C@Au-CTAB$	0.25 mg L^{-1}	1 mg	1.870	25
$\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$	2 mL, 10 mg L^{-1}	0.25 mg mL^{-1} , 200 μL (0.05 mg)	3.510	This work

Table 4 Comparison of the RhB catalytic degradation performance of different catalytic materials

Sample	RhB	Catalyst dosage	k (min^{-1})	Ref.
F- CeO_2/CdS	50 mL, 10 mg L^{-1}	50 mg	0.036	43
$\text{BN}/\text{C}_3\text{N}_4$	50 mL, 5 mg L^{-1}	100 mg	0.072	44
$\text{Pd}-\text{TiO}_2/\text{Bi}_2\text{O}_3$	10 mg L^{-1}	50 mg	0.110	45
$\text{Fe}_3\text{O}_4@C@Au-CTAB$	0.25 mg L^{-1}	1 mg	0.500	25
$\text{Fe}_3\text{O}_4@PGFR@Ag-CTAB$	2 mL, 10 mg L^{-1}	0.25 mg mL^{-1} , 200 μL (0.05 mg)	0.103	This work



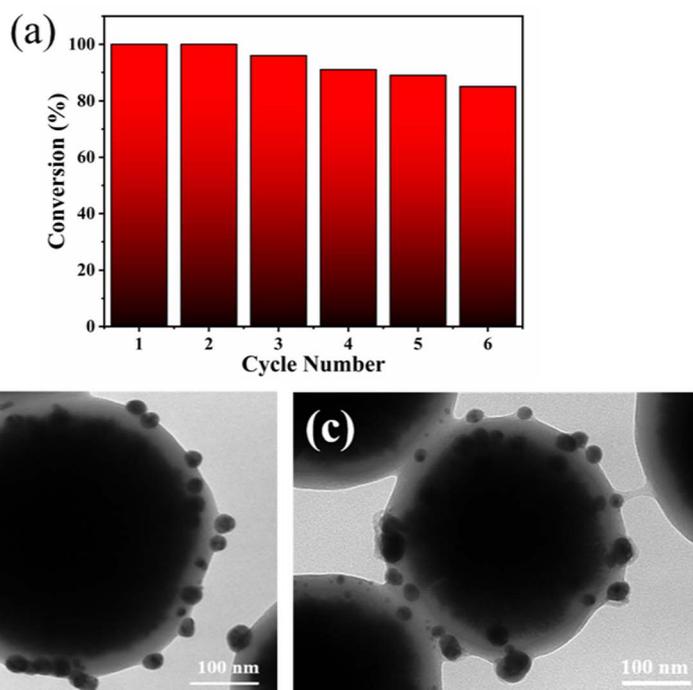


Fig. 11 Cycle performance. (a) Catalytic reuse efficiency. TEM images of Fe₃O₄@PGFR@Ag-CTAB (b) before the cycle and (c) after six cycles.

cycling experiments were carried out. As shown in Fig. 11a, Fe₃O₄@PGFR@Ag-CTAB nanoparticles exhibited an efficient catalytic capacity for MO, which was sustained at approximately 85%. This indicated that Fe₃O₄@PGFR@Ag-CTAB nanoparticles possessed an effective cycling capacity and stability for MO. Furthermore, as shown in Fig. 11c, after multiple cycles, the Ag NPs in Fe₃O₄@PGFR@Ag-CTAB nanoparticles did not exhibit significant shedding and the structure remained intact. The sustainability of catalytic materials was confirmed by the presence of silver nanoparticles and the integrity of the core-shell structure. The cyclic tests demonstrated that PGFR was an ideal carrier for Ag NPs, which could achieve the efficient and continuous chelation and anchoring of Ag NPs. The CTAB-modified Fe₃O₄@PGFR@Ag nanoparticles maintained efficient catalytic activity for MO in cycling tests, and the structure of the catalytic materials remained intact during the reaction process.

4. Conclusions

In this work, Fe₃O₄@PGFR@Ag core-shell nanomaterials were successfully prepared with controlled charge switching using a facile CTAB modification method. Fe₃O₄@PGFR@Ag-CTAB exhibited efficient catalytic properties towards the anionic dye MO, which was attributed to favorable electrostatic interactions. The catalytic rate constant of Fe₃O₄@PGFR@Ag-CTAB for MO was found to be 3.510 min⁻¹, 124% higher than that of Fe₃O₄@PGFR@Ag. Similarly, the *k* value for the cationic dye RhB of Fe₃O₄@PGFR@Ag was 2.83 min⁻¹, which was 90% higher than that of positively charged Fe₃O₄@PGFR@Ag-CTAB. Moreover, Fe₃O₄@PGFR@Ag and Fe₃O₄@PGFR@Ag-CTAB showed similar

catalytic degradation efficiencies towards the neutral antibiotic TC. These results demonstrated that the catalytic activity was not only dependent on the property of the catalyst but also on the charge state of the contaminant.

Data availability

The authors affirm that the data supporting the findings of this study are included in the article. Additional data can be made available from the corresponding author upon reasonable request.

Author contributions

Liping Jiang: data curation, formal analysis, methodology, and writing – original draft. Yang Xi: data curation, formal analysis, and writing – review & editing. Ziyi Xu: investigation and methodology. Zewen Song: investigation and methodology. Yuwei Cui: formal analysis and investigation. Haijun Zhou: data curation, funding acquisition, project administration, supervision, and writing – review & editing.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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