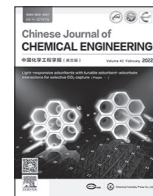




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Full Length Article

Simultaneous degradation of RhB and reduction of Cr(VI) by MIL-53(Fe)/Polyaniline (PANI) with the mediation of organic acid

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ABSTRACT

MIL-53(Fe)/polyaniline (PANI) composite was prepared by *in situ* depositing PANI on the surface of MIL-53(Fe) and their catalytic performances on the simultaneous removal of RhB and Cr(VI) were investigated. The elimination efficiency of both RhB and Cr(VI) reached more than 98% under pH = 2 where hydrochloric acid and citric acid were used to adjust the pH. The results indicated that MIL-53(Fe)/PANI revealed an obvious pH response to the degradation of RhB, while citric acid promoted the Cr(VI) photoreduction. UV-Vis spectra, EIS, and photocurrent response experiments showed that MIL-53(Fe)/PANI had a better light response and carrier migration ability than MIL-53(Fe). The transient absorption spectra also exhibited that the lifetimes of photo-generated carriers were prolonged after the conductive polymer deposition on the MIL-53(Fe) surface. Scavenger experiments demonstrated that the main active species were $\cdot\text{O}_2^-$ and $\cdot\text{OH}$. Combined with activity evaluation results, and the possible photocatalytic mechanism of MIL-53(Fe)/PANI on RhB oxidation and Cr(VI) reduction was proposed. The addition of conductive polymer can effectively improve the light response of the catalyst under acidic conditions, and meanwhile citric acid also provided a new mediation for the synergistic degradation of multiple pollutants. Good activity and stability of the catalysts made the scale-up purification of acid water feasible under UV-Vis light.

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1. Introduction

The water environment is intimately tied to human health. These days, water pollution has become a serious problem, and many technologies have been used for water environment remediation, such as adsorption [1,2], biological oxidation [3], electrochemical oxidation [4], sonochemical pyrolysis [5], microwave-Fenton [6,7], and photocatalytic redox processes [8–10]. Among these methods, the photocatalytic technique offers advantages because of its low cost, low toxicity and renewability. Hexavalent chromium [Cr(VI)] is widely used in dye synthesis industry, and there may be both hexavalent chromium and industrial dyes in sewage [11]. Simultaneous treatment of chromium (VI) and dyes (e.g. RhB) by photocatalytic oxidation thus could be very useful and it has attracted attention [12,13]. However, constructing an effective photocatalytic system that achieves the dual functions of photocatalytic oxidation and reduction remains a challenge.

Therefore, it is essential and urgent to fabricate new effective photocatalysts for synergetic removal of pollutant's removal.

As a new kind of functional material, metal-organic frameworks (MOFs) have a variety of excellent properties, including high specific surface area, controllable pore size, and post-synthetic modification [14]. At present, MOFs have attracted wide attention in gas adsorption/separation [15], sensing [16], electronic devices [17], heterogeneous Catalysis [18–22], and so on. MIL-53(Fe) is a widely studied Fe-based MOF that shows a good response to UV and visible light. It can be used as a photocatalyst for organic pollutants degradation and Cr(VI) reduction [23]. Tirusew Araya [24] *et al.* modified MIL-53(Fe) with resin and showed excellent photodegradation ability to dye wastewater such as rhodamine B (RhB) and methylene blue (MB). Hu [25] *et al.* deposited CdS nanoparticles on the surface of MIL-53(Fe) to improve the degradation of RhB. Wu [26] *et al.* studied for the first time that using MIL-53(Fe) for reduction of Cr(VI) and degradation of dyes simultaneously. It has been proved that MIL-53(Fe) could play as a redox bifunctional photocatalyst and a promising material for environmental remediation. However, its application in photocatalytic wastewater treatment is limited by its poor water stability, poor

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electrical conductivity, and fast recombination of photogenerated electron holes.

Polyaniline (PANI) is a kind of conductive polymer with low cost, easy synthesis, and high conductivity. The π or π^* bond orbitals of PANI can produce charge transfer through charge transfer complexes [27]. Surface hybridization only occurs on the monolayer with chemical bonding, which is photocatalytic stable and will not be degraded by photocatalysis. Previous reports had shown that surface modification of the semiconductor materials such as TiO_2 [28], $\text{g-C}_3\text{N}_4$ [29], and MOFs materials such as MIL-101(Fe) [30], MIL-88A(Fe) [31] with PANI, could significantly improve their photoresponse performance. Surface hybridization of PANI on the photocatalyst can not only improve the photocatalytic performance but also inhibit the photocorrosion effect and produce visible light activity.

Organic acids such as oxalic acid, citric acid, and tartaric acid can affect the redox properties of Cr(VI) . It has been reported that citric acid can reduce Cr(VI) to Cr(III) directly under light [32]. Short-chain hydrocarbons such as oxalic acid, citric acid, and tartaric acid can be added to the photocatalytic reaction system to capture photogenerated holes to improve the efficiency of photocatalytic reduction [33]. The structure of organic acid has a significant effect on reaction efficiency. It has been reported that the number of $\alpha\text{-OH}$ in organic acids is the key factor to determine the reduction performance of Cr(VI) [34,35]. Sun *et al.* [36] shown that the number of carboxyl groups also affects the degradation efficiency of ronidazole. The pH value of the reaction system may also significantly affect the photocatalytic efficiency as the electrode potential of the Cr(VI)/Cr(III) pair is related to the pH of the solution [37]. The higher the pH value, the more negative the electrode potential, the weaker the oxidizability of Cr(VI) in the system, which is not conducive to its reduction. Meanwhile, PANI has a characteristic of reversible doping effect and has an apparent response to pH [38], which may benefit the redox process via a synergistic effect.

Herein, we successfully prepared a composite photocatalyst, named as MIL-53(Fe)/PANI, by in situ depositing PANI on the surface of MIL-53(Fe) and their catalytic performances on the simultaneous removal of RhB and Cr(VI) were investigated. The pH value was regulated with hydrochloric acid and citric acid. The separation efficiency of photogenerated carriers was studied by transient photocurrent (TPC) measurement and electrochemical impedance spectroscopy (EIS). The photogenerated carriers' lifetimes were characterized by the transient absorption spectrum (TAS). Based on the trapping agent experiments and kinetic study, the possible reaction mechanism was put forward. This work provides a new idea for the photocatalytic treatment of contaminants in acid wastewater synergistically.

2. Materials and Methods

2.1. Catalyst preparation

Preparation of MIL-53(Fe). As indicated in the published literature [39], the solvothermal method was adopted to prepare MIL-53(Fe). 2.703 g (10 mmol) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.66 g (10 mmol) H_2BDC dissolved in 56 ml DMF and stirred for 1 h. The solution was transferred to a 100 ml volume of PTFE lined reactor and kept at 150 °C for 24 h. The samples were collected by centrifugation, washed many times with DMF and ethanol, stirred in 250 ml deionized water for 8–9 h, and the collected products were dried at 120 °C for 12 h.

Preparation of PANI. 100 μl aniline ($\text{C}_6\text{H}_7\text{N}$) was dissolved in 50 ml 1 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 and mixed uniformly at room temperature, marked as solution A. At the same time, 0.25 g of ammonium

persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) is completely dissolved in 50 ml 1 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 solution, which is recorded as solution B. The molar ratio of aniline monomer to ammonium persulfate was 1:1, and solutions A and B were cooled in the ice water bath for 1 h. In an ice bath, solution B was added to solution A and stirred for 4 h to form a dark green viscous PANI solution. The filter collection products are washed with deionized water and then dried and set aside.

Preparation of MIL-53(Fe)/PANI. The preparation method for MIL-53(Fe)/PANI is similar to that of PANI (Fig. 1). When solution B is added to solution A, 1 g of prepared MIL-53(Fe) was added and stirred in an ice bath for 4 h. The filter collection product was washed with deionized water and dried.

2.2. Catalyst characterizations

Bruker D8-ADVANCE diffractometer was used to analyze the crystallinity of as-prepared samples with a source of Cu K_α radiation and the 2 theta at a scan rate of $4^\circ\cdot\text{min}^{-1}$ ranges from 10° to 40° . ZEISS GeminiSEM 500/300 scanning electron microscope was used to characterize the surface morphology. U4100 (Hitachi High-tech Co.) was used to study the UV–Vis spectra of samples with the scanning range of 200–800 nm on the scan speed of $300\text{ nm}\cdot\text{min}^{-1}$. The characteristics of N_2 adsorption–desorption isotherms and pore properties at 77 K (liquid nitrogen temperature) were obtained by BSD-PM2.

2.3. Electrochemical measurements

An electrochemical analyzer (Chenhua CHI-660E, Shanghai) was used to test the photoelectrochemical properties in a typical three-electrode cell. The electrolyte, counter, and reference electrodes were respectively Na_2SO_4 solution ($0.5\text{ mol}\cdot\text{L}^{-1}$), a platinum wire, and an Ag/AgCl electrode. The working electrode was made of ITO electrodes deposited with samples. The preparation method was as follows: The samples were dissolved in 0.15 ml ethanol, then 15 ml naphthol was added and ultrasonically processed for 30 minutes. The 15 μl supernatant was used to coat ITO glass ($15\text{ mm} \times 15\text{ mm}$) with a $10\text{ mm} \times 10\text{ mm}$ area.

2.4. Nanosecond transient absorption spectroscopy

Transient absorption spectrum (TAS) was recorded on an LFP1000 spectrometer (nanosecond transient absorption

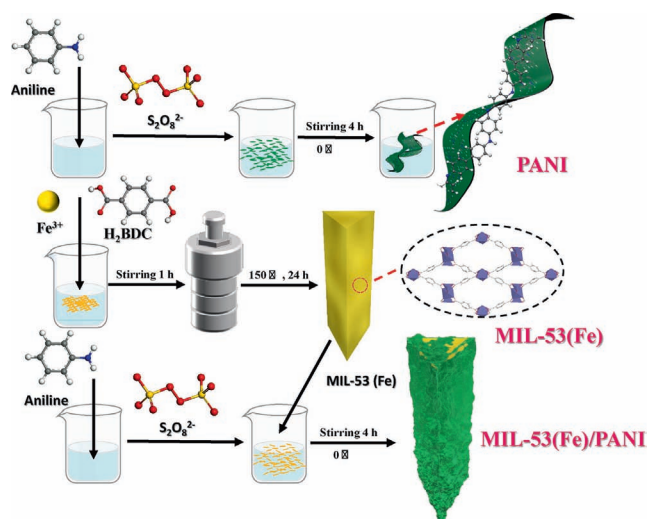


Fig. 1. Schematic illustration of the fabrication process for PANI, MIL-53(Fe), and MIL-53(Fe)/PANI.

spectroscopy, NTAS) in the air at room temperature. A 450 W Xe lamp was used as a probe light. A Nd:YAG nanosecond laser system (Beamtech Optronics Co., Ltd.) with output of 12 mJ at 355 nm, operating at the repetition rate of 3 Hz were used as the excitation source.

2.5. Photocatalytic activity

RhB degradation and Cr(VI) reduction in an aqueous solution with a jacket reactor measured the photocatalytic activity of catalysts. Xe lamp (300 W) with the full spectrum (300–780 nm) as irradiation source, and all tests were carried out at room temperature in the air by water circulation. The photocatalyst ($1 \text{ g} \cdot \text{L}^{-1}$) was added to an aqueous solution of RhB (100 mL , $10 \text{ mg} \cdot \text{L}^{-1}$) and/or Cr(VI) (100 mL , $10 \text{ mg} \cdot \text{L}^{-1}$). After regulated the pH with $2 \text{ mol} \cdot \text{L}^{-1}$ hydrochloric to or solid citric acid monohydrate (CAM) to 2, 3, 4, and 6, respectively. Before irradiation, the suspension was stirred in the dark for 60 min to reach the adsorption–desorption equilibrium. After that, 4 mL of the solution was collected every 20 min under light, and the photocatalyst was separated by centrifugation at a speed of $5000 \text{ r} \cdot \text{min}^{-1}$. Measure the content of Cr(VI) and RhB with a transparent solution through an ultraviolet–visible spectrometer. The maximum absorbance wavelength of Cr(VI) and RhB were 356 nm and 554 nm.

3. Results and Discussion

3.1. Photocatalytic activity

Simultaneous Removal of RhB and Cr(VI). The catalytic performances of as-prepared samples were evaluated by simultaneous removal of RhB ($10 \text{ mg} \cdot \text{L}^{-1}$) and Cr(VI) ($10 \text{ mg} \cdot \text{L}^{-1}$). Under the condition that the initial pH value of the solution was constant, MIL-53(Fe) and MIL-53(Fe)/PANI were used to remove the RhB and Cr(VI) respectively. The experimental results showed (Fig. 2a) that light alone had almost no effect on the reduction of Cr(VI), but the degradation of RhB reached 24% within 120 min. The photocatalytic effect of composite catalyst MIL-53(Fe)/PANI was better than that of pure MIL-53(Fe), and the elimination of RhB and Cr(VI) can up to 61% and 33%, respectively. This was consistent with the experimental results of the photocurrent and EIS. When used MIL-53(Fe)/PANI to simultaneous remove RhB and Cr(VI) (Fig. 2b), the degradation of RhB increased from 61% to 75% within 120 min, and the reduction of Cr(VI) increased from 33% to 38%. This suggests that there is a synergistic effect in the photocatalytic processes of the simultaneous reduction of Cr(VI) and oxidation of RhB. It is suspected that Cr(VI) can consume photoelectrons, promoting the separation of photogenerated electrons from holes.

The effect of initial pH. MIL-53(Fe)/PANI showed a very significant response to pH (Fig. 2c). After adjusting the pH value with 2 M HCl, the degradation of RhB increased significantly, from 55% (at pH = 6) to 96% (at pH = 2) in 80 min. However, the reduction of Cr(VI) was not significantly improved, and the elimination was still about 30%. It has been reported that citric acid can promote the photoreduction of Cr(VI) [32]. Using only citric acid to adjust the pH of the solution without catalyst, the reduction of Cr(VI) can reach 96% within 20 min (Fig. 2d). Citric acid was also able to ameliorate the photocatalytic effect of MIL-53(Fe)/PANI, which still achieved 75% degradation of a single pollutant RhB at pH = 2 (Fig. 2e). For the simultaneous removal of two pollutants, the elimination of RhB and Cr(VI) can up to 75% and 98%, respectively (Fig. 2f). Considering the promotion of HCl on the degradation of RhB, we used HCl and citric acid together to adjust the pH of the solution, and the elimination of both RhB and Cr(VI) reached over 98% when pH = 2 (Fig. 2g). The possible reason is that the H^+ disso-

ciated by citric acid can promote the charge transfer rate of MIL-53(Fe)/PANI, while citric acid itself generates electrons under photoexcitation and participates in the reduction reaction of Cr(VI) [40].

Effect of initial concentration and stability of the catalyst. Different initial concentrations of pollutants were used to evaluate the photocatalytic effect of MIL-53(Fe)/PANI separately. The maximum removal of Cr(VI) was essentially unchanged when the concentration was inclined from $10 \text{ mg} \cdot \text{L}^{-1}$ to $40 \text{ mg} \cdot \text{L}^{-1}$, while the degradation of RhB decreased from 98% to 68% (Fig. 2h). These might be attributed to the fact that the amount of reactive oxygen species (ROS) is not sufficient to fully oxidize the adsorbed RhB. The stability of the MIL-53(Fe)/PANI was also investigated, and the elimination of RhB and Cr(VI) was 84% and 89% respectively after four cycles (Fig. 2i). The removal of RhB and Cr(VI) recovered to 95% after washing by immersion in acidic solution, exhibiting good stability.

Kinetic studies. The reaction kinetics for the removal of RhB and Cr(VI) were calculated (Fig. 3), and the fitting results were in accordance with the pseudo first-order kinetics model. When degrading a single pollutant, and MIL-53(Fe)/PANI was applied as the catalyst, the degradation rate of RhB was 0.0072 min^{-1} , and slightly increased to 0.0086 min^{-1} when citric acid was applied for pH adjustment. Interestingly, in the case of the co-existence of RhB and Cr(VI), the rate of degradation of RhB was 0.0485 min^{-1} and the rate of reduction of Cr(VI) was 0.0012 min^{-1} when pH was adjusted using HCl. While citric acid was used to adjust pH, the degradation rate of RhB increased to 0.01 min^{-1} and the reduction rate of Cr(VI) increased to 0.2575 min^{-1} . The rate of contaminant removal decreased when pH was adjusted with both HCl and citric acid, with 0.0133 min^{-1} for RhB and 0.0532 min^{-1} for Cr(VI). Overall, MIL-53(Fe)/PANI exhibited the best photocatalytic performance with pH = 2 adjusted with citric and hydrochloric acids for the simultaneous removal of RhB and Cr(VI).

3.2. Catalyst characterizations

The as-prepared MIL-53(Fe) exhibited the typical characteristic peaks at 12.63° , 17.54° , 18.13° , 25.37° , and 27.23° (Fig. 4a), which accorded well with the previously reported MIL-53(Fe) as well as the simulated one [41]. It demonstrated that MIL-53(Fe) had been successfully prepared. After in situ deposition of PANI in MIL-53(Fe), the characteristic peaks belonging to MIL-53(Fe) were still observed, indicating that the composite of MIL-53(Fe) and PANI was successful and the crystal structure was intact.

The light absorption properties of the catalysts are usually evaluated by UV–Vis DRS. It can be seen from Fig. 4b that MIL-53(Fe) absorbs visible light well in the 400–600 nm range. There was also a small peak at 450 nm that belongs to the spin-allowed d–d transition (${}^6\text{A}_{1g} \Rightarrow {}^4\text{A}_{1g} + {}^4\text{E}_g(\text{G})$) in Fe(III) [42]. After the introduction of PANI, it can be seen that the absorption edge of the composite catalyst has an apparent red shift. The possible reason was that the conjugation degree of the whole system increased, and the strong interaction between PANI and MIL-53(Fe) makes the electron cloud tend to average [43]. The energy band gap (E_g) of the photocatalysts can be calculated using $\alpha(h\nu) = A(h\nu - E_g)^{n/2}$, where α , h , ν , and A represents the absorption coefficient, Planck's constant, the light frequency and a constant, respectively. The energy gap of MIL-53(Fe) and MIL-53(Fe)/PANI were calculated as 2.63 and 2.27 eV, respectively (Fig. 4c). Compared with MIL-53(Fe), the energy gap of MIL-53(Fe)/PANI was narrowed after the introduction of PANI. The relatively narrow band gap energy of MIL-53(Fe)/PANI composites could be attributed to the strong interactions of the hybrid structures formed between MIL-53(Fe) and PANI, which makes better use of visible light to boost photocatalysis performance [30].

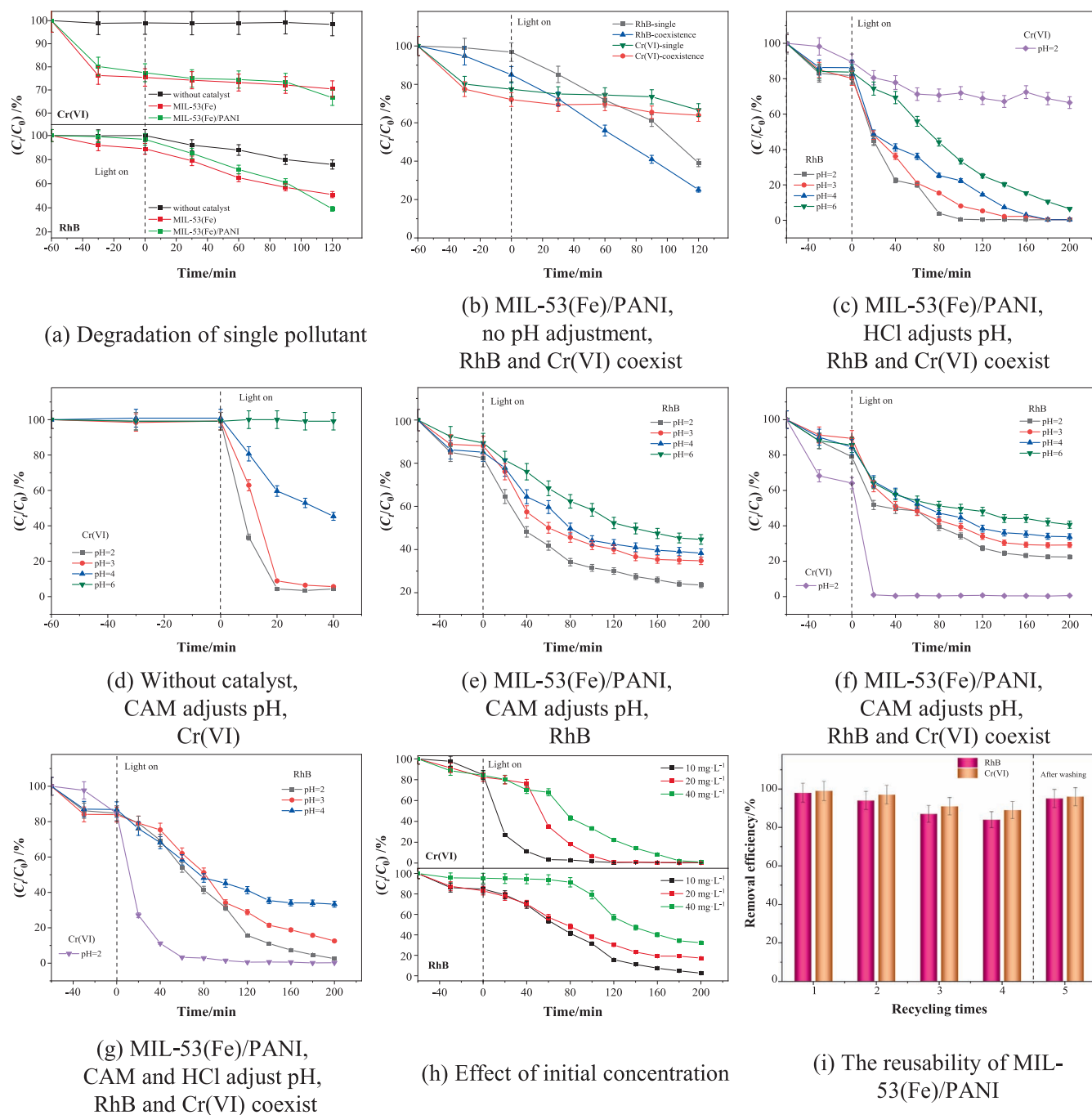
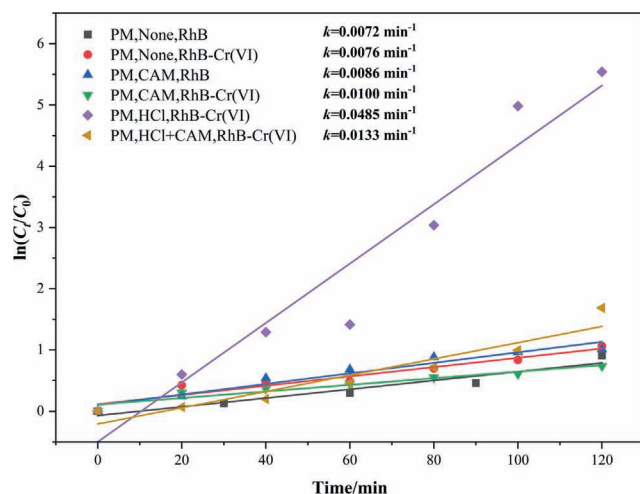


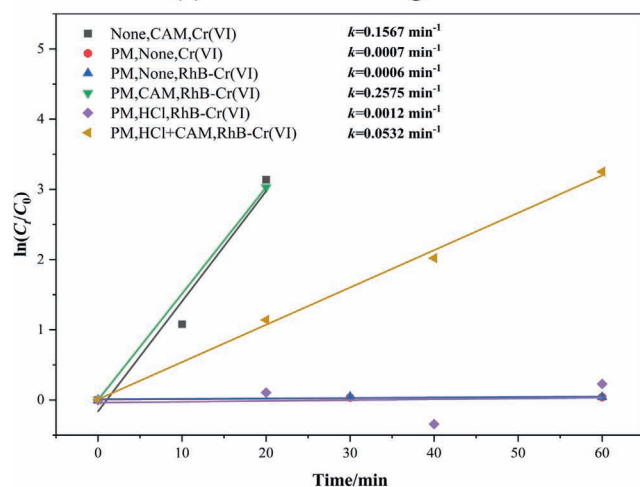
Fig. 2. Photocatalytic removal curves under UV-Vis irradiation.

As shown in Fig. 5a and b, MIL-53(Fe) displayed a triangular prism-like structure, where the micro-rods had a width of 15–30 μm and the lengths of several tens of micrometers. After in situ deposition of PANI, the surface of MIL-53(Fe) becomes rough but still maintains an apparent triangular prism-like structure, indicating that the introduction of polyaniline has little effect on the morphology of MIL-53(Fe) and combines well with the surface of MIL-53(Fe). In addition, the EDS elemental analysis was shown in Fig. 5c–f revealed the presence of N, O, and Fe elements in MIL-53(Fe)/PANI. From the N element distribution, it can be seen that PANI was uniformly deposited on the surface of MIL-53(Fe) [44].

The N_2 adsorption–desorption isotherms for MIL-53(Fe) and MIL-53(Fe)/PANI were displayed in Fig. 6a, and two catalysts exhibited a typical IV type adsorption isotherm containing a hysteresis loop. The pore size distribution (PSD) curves also indicated that both of the samples possessed two peaks in Fig. 6b,c, demonstrating their mesoporous structure [45]. Table 1 summarizes the specific surface area, total pore volume, and pore size distribution of as-prepared catalysts according to Barrett-Joyner-Halenda (BJH) method. The BET surface area of MIL-53(Fe)/PANI was less than pure MIL-53(Fe). The total pore volume of MIL-53(Fe)/PANI ($0.0395 \text{ cm}^3 \cdot \text{g}^{-1}$) was also lower than pure MIL-53(Fe) ($0.0489 \text{ cm}^3 \cdot \text{g}^{-1}$). The curve for the MIL53(Fe)/PANI exhibits a dual-porosity



(a) The kinetic fittings of RhB



(b) The kinetic fittings of Cr(VI)

Fig. 3. The Kinetic fitting curves.

structure with one peak occurring at a pore radius of 3.81 nm and another peak occurring at 49.07 nm, while the two peaks for MIL-53(Fe) were at 3.83 and 28.58 nm. It is possible that when the aniline was *in situ* polymerized on the MIL-53(Fe) surface, covered some of the pores of MIL-53(Fe), and caused a reduction in specific surface area and pore volume. This was confirmed in Fig. 2a that the adsorption performance of MIL-53(Fe)/PANI for pollutants (in the dark) was less than that of pure MIL-53(Fe).

3.3. Photoelectrochemical analysis

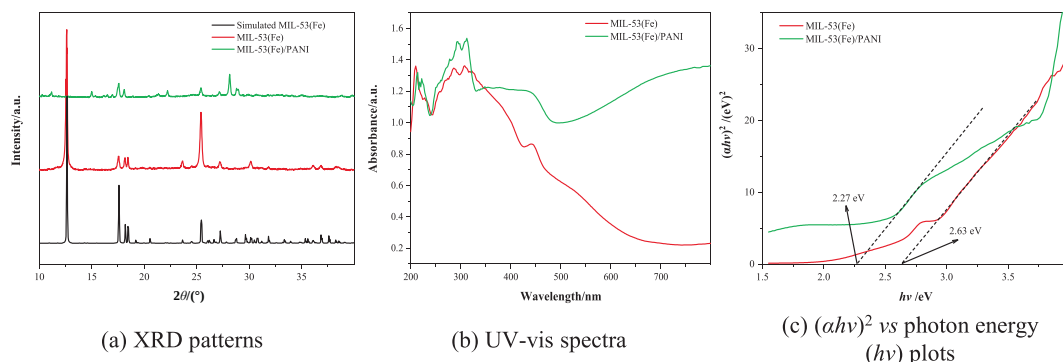
Transient photocurrent responses were determined to investigate the photoelectric responses of the Catalysts. As can be seen from Fig. 7a, a significant change in the current response can be observed when visible light was turned off to on. The MIL-53(Fe)/PANI produced a much higher photocurrent than both MIL-53(Fe) and PANI under the same conditions. The enhanced photocurrent indicated that the separation efficiency of photogenerated electron-hole pairs was much higher by adding PANI. It was conducted that a helpful modified material was fabricated successfully, which facilitated the rapid transfer and separation of photoinduced carriers. The highly enhanced photocurrent response of MIL-53(Fe)/PANI may be attributed to the superior charge mobility derived from the π -conjugation in the PANI structure [46].

The charge transfer behavior of the catalyst was further analyzed by electrochemical impedance spectroscopy (EIS). Typically, because of the more efficient separation of photogenerated electron-hole pairs and faster interface charge transfer, a smaller arc radius in the EIS spectra suggests low photoelectrode charge transfer resistance. As depicted in Fig. 7b, composite catalyst resulted in the shortest arc radius compared with the two pure materials, implying that the MIL-53(Fe)/PANI photo-electrode exhibited the fastest interfacial charge transfer and the most efficient separation of photo-generated charge carriers compared with pure MIL-53(Fe) and PANI [47].

The positive slope of the Mott-Schottky curve for MIL-53(Fe) indicates that MIL-53(Fe) was an n-type semiconductor with the flat band potential of -0.33 V versus Ag/AgCl (Fig. 7c), which could be deemed as conduction band potentials [48]. Moreover, according to the relationship between NHE and Ag/AgCl reference potentials, the conduction band potentials (E_{CB}) of pristine MIL-53(Fe) was calculated to be -0.13 V versus NHE, which is more negative than that of Cr^{6+}/Cr^{3+} ($+1.12$ V, pH = 2) and can reduce Cr(VI) to Cr(III) [49]. Combining with the band gap energy calculated from UV-Vis DRS and the empirical formula of $E_g = E_{VB} - E_{CB}$, the valence band position (E_{VB}) of MIL-53(Fe) was computed to be 2.50 V vs NHE. According to the literature, the LUMO and the HOMO potentials of PANI are -2.1 and 0.62 V, respectively [50]. The LUMO orbital potential of PANI is more negative than that of O_2/O_2^- (-0.33 V) [51], which can reduce O_2 to superoxide radicals ($\cdot O_2^-$) and participate in the reaction.

3.4. Charge transfer characterization

After the photocatalyst is irradiated by light, the electrons in the ground state will be excited and transition to a higher energy level and leaving holes. If there is no foreign electron receiver, the excited electrons will return to the ground state and recombine

Fig. 4. XRD patterns, UV-vis spectra and $(\alpha h\nu)^2$ vs photon energy ($h\nu$) plots for MIL-53(Fe) and MIL-53(Fe)/PANI.

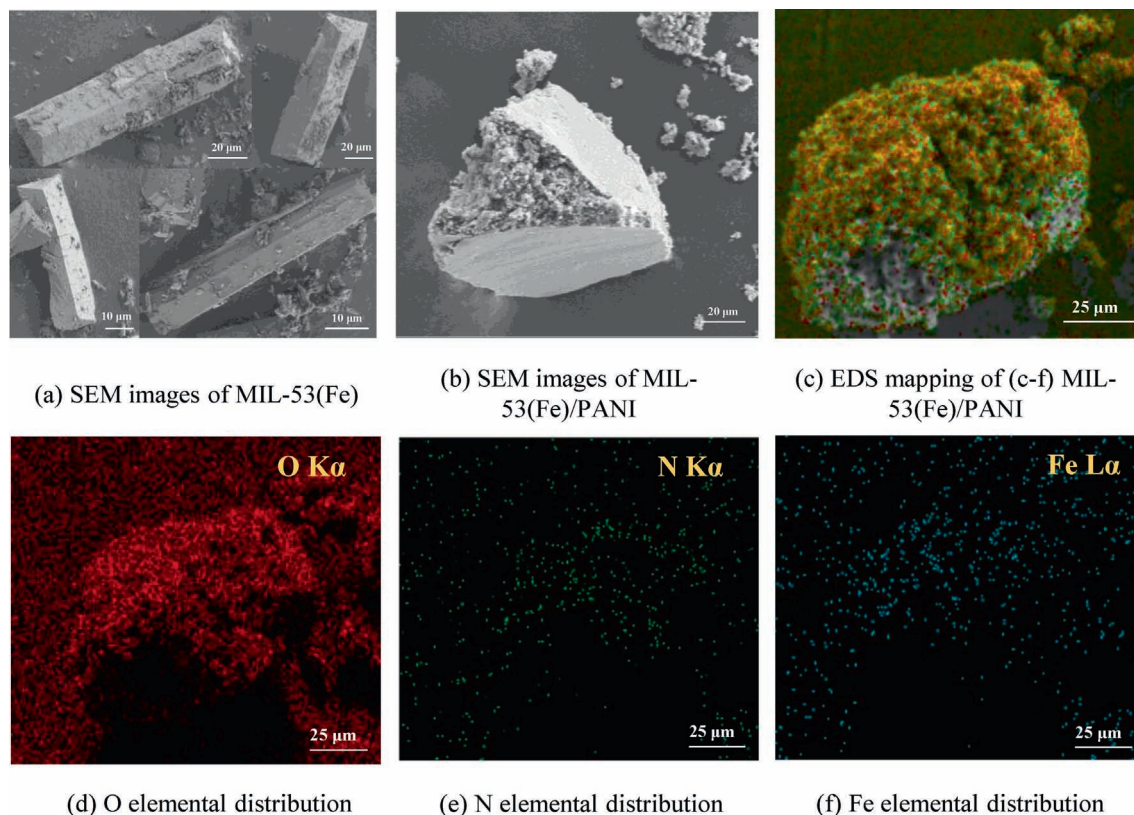


Fig. 5. SEM images of MIL-53(Fe) and MIL-53(Fe)/PANI, and corresponding EDS mapping of MIL-53(Fe)/PANI.

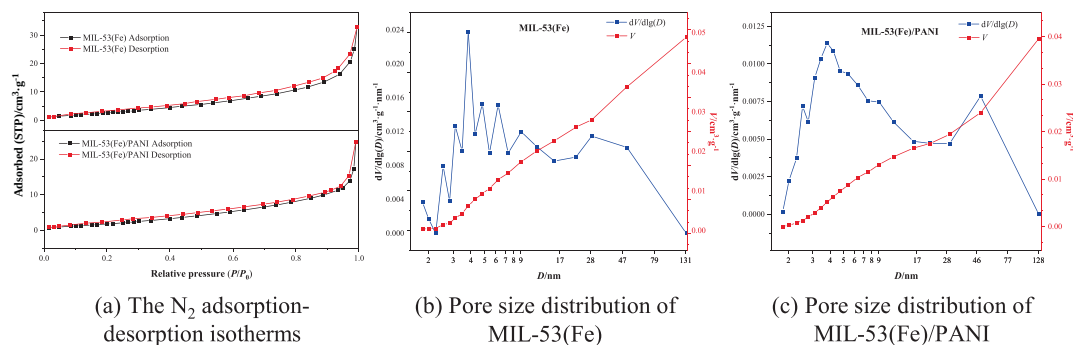


Fig. 6. The N_2 adsorption-desorption isotherms and pore size distribution of the samples.

Table 1
Physicochemical parameters of the photocatalysts

Samples	$S_{BET}/m^2 \cdot g^{-1}$	Total pore volume/ $cm^3 \cdot g^{-1}$	PSD (Dual-porosity structure)/nm
MIL-53(Fe)	12.1991	0.0489	3.8316/28.5761
MIL-53(Fe)/PANI	8.6869	0.0395	3.8106/49.0696

with the hole to emit fluorescence signals, or be captured by the nearby electron capture state, maintain the high energy state, and then return to the ground state to recombine [52]. To further understand the lifetime of photogenerated carriers, transient absorption spectra (TAS) measurements were carried out. We observed obvious curve oscillations on the nanosecond time scale and used the following formula for global fitting (Fig. 8a) [53]:

$$y = A \times \exp(-t/\tau) + y_0 \quad (1)$$

where t is time, τ is the global lifetime of the excited state, A is the relative absorption intensity. For the MIL-53(Fe), the lifetime of the excited state was fitted to be (194.5 ± 6.5) ns with the R^2 of 0.9302. Moreover, the excited state lifetime of MIL-53(Fe)/PANI was fitted to (208.6 ± 7.0) ns with the R^2 of 0.9313. It indicated that the recombination process of photogenerated electrons and holes in MIL-53(Fe)/PANI was slower, and the lifetime of photogenerated electrons at high energy levels was longer than that in MIL-53(Fe). It may be that after the introduction of PANI, the π - π conjugated system expands the delocalization range of electrons so that the recombination process becomes slow without external electron acceptors [43].

3.5. Possible photocatalytic mechanism

The scavenger experiments of reactive species were carried out to better understand the main active species in the photocatalytic

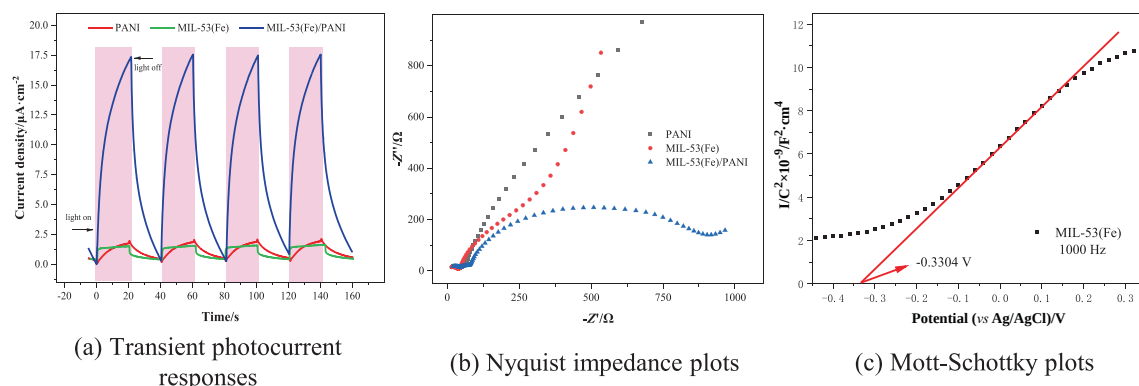
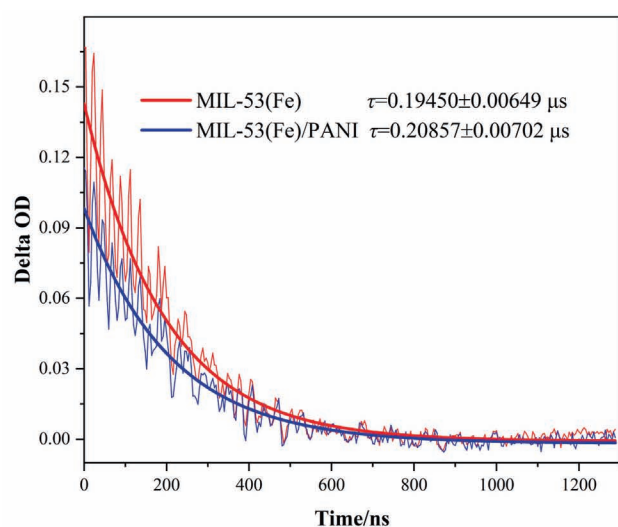


Fig. 7. Transient photocurrent responses, Nyquist impedance plots, and Mott-Schottky plots of the samples.



(a) Transient absorbance spectra and their fittings excited by 12 mJ@355 nm at 370 nm

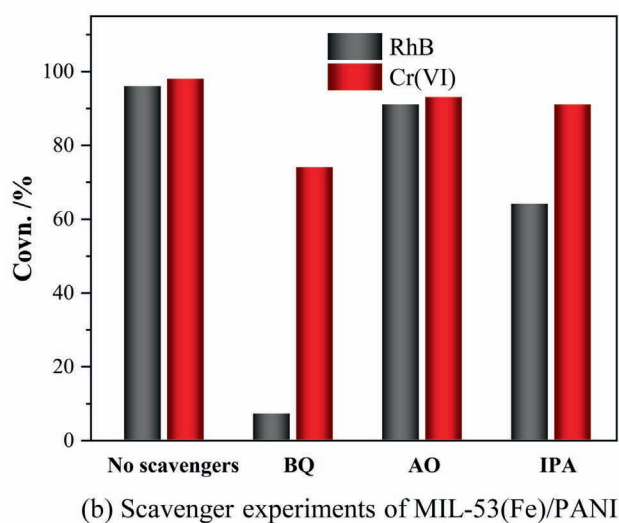


Fig. 8. Transient absorbance spectra and scavenger experiments.

process (Fig. 8b). The scavengers Isopropanol (IPA), p-benzoquinone (PBQ), and ammonium oxalate (AO) made an addition to the RhB/Cr(VI) solution to trap the hydroxyl radical ($\cdot\text{OH}$),

superoxygen radicals ($\cdot\text{O}_2^-$) and the holes (h^+) [8]. It can be seen that after the addition of BQ, the degradation efficiency of RhB was greatly reduced to less than 10%. After added IPA, the degradation efficiency of RhB also decreased to 64%. However, the degradation efficiency of RhB was the same as that without trapping agent (~95%) after AO adding. The results showed that $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ were the main active species in the process of photocatalytic degradation of RhB. In addition, only with the addition of BQ, the reduction efficiency of Cr(VI) decrease, indicating that superoxide radical is the main active species for the reduction of Cr(VI).

Both PANI and MIL-53(Fe) generated electrons (e^-) under light excitation. The potential of the lowest unoccupied molecular orbital (LUMO) of PANI is more negative than that of MIL-53(Fe), and the e^- produced by PANI can be easily transferred to the CB of MIL-53(Fe). However, the CB potential of MIL-53(Fe) is more positive than that of $\text{O}_2/\cdot\text{O}_2^-$ (-0.33 V), and $\cdot\text{O}_2^-$ cannot be produced. The trapping agent experiment confirmed that $\cdot\text{O}_2^-$ was the main contributing species, which was not consistent with the experimental results. Therefore, the traditional type II photogenerated carrier transport mechanism is not suitable to explain the mechanism here. On this basis, we proposed a possible reaction mechanism (Fig. 9). Under light excitation, the e^- excitation in the VB of the MIL-53(Fe) transitions to the CB, leaving a h^+ in the VB, and the e^- on the highest occupied molecular orbital (HOMO) of PANI transitions to the LUMO (Eq. (2)). The energy gap (2.01 eV) between the

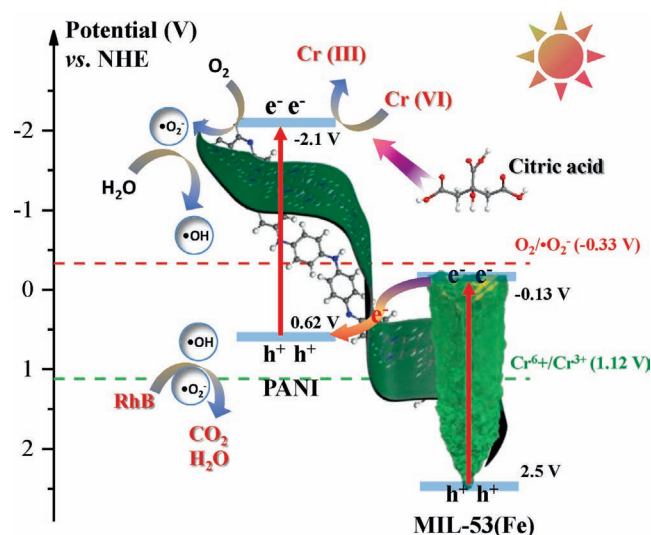
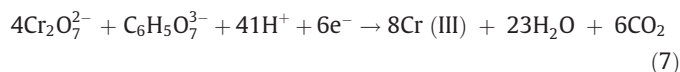
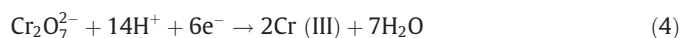


Fig. 9. Possible photocatalytic mechanism of photocatalytic RhB degradation and Cr (VI) reduction.

LUMO of PANI and the CB of MIL-53(Fe) is larger than the energy gap (0.75 eV) between the CB of MIL-53(Fe) to the HOMO of PANI. Therefore, the e^- of MIL-53(Fe) is more easily consumed by combining with the h^+ in the HOMO of PANI. The e^- on the LUMO of PANI reduces the dissolved O_2 in water to $\cdot O_2^-$ (Eq. (3)) and directly reduces Cr(VI) (at low pH values, $Cr_2O_7^{2-}$ ions are the main species [11]) to Cr(III) (Eq. (4)) [54]. Moreover, $\cdot O_2^-$ also reacts with water to form $\cdot OH$ (Eq. (5)). The $\cdot OH$ and $\cdot O_2^-$ participate in the degradation of RhB simultaneously (Eq. (6)). However, it has been reported that the lone pair electrons of hydroxyl groups on citric acid carboxyl groups are excited due to their inherent electron-rich properties under UV irradiation (300–400 nm) [40]. The excited e^- enters the empty d orbitals of Cr(VI) and reduces Cr(VI) to Cr(III). So there is another pathway for the reduction of Cr(VI), where the excited citric acid with e^- reduces Cr(VI) to Cr(III) and is itself oxidized to CO_2 (Eq. (7)) [40].



4. Conclusions

In summary, MIL-53(Fe)/PANI revealed an obvious pH response to the degradation of RhB, while citric acid played a direct effect on the Cr(VI) photoreduction. When the pH was regulated with hydrochloric acid and citric acid to 2.0, the RhB and Cr(VI) removal rate reached more than 95% under ultraviolet–visible light irradiation for 200 min. The UV–Vis diffuse reflectance spectra of the MIL-53(Fe)/PANI show they can broaden the absorption of light, and their EIS, photocurrent response and transient absorption spectra reveal that the photogenerated carriers produced by MIL-53(Fe)/PANI have faster migration rate and longer lifetime than MIL-53(Fe). The scavenger experiments demonstrated that $\cdot O_2^-$ and $\cdot OH$ were the main active species, so we put forward the possible electron transfer mechanism and reaction mechanism, which provides a new idea for the synergistic treatment of acid wastewater.

Declaration of Competing 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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