NH$_2$-MIL-88B (Fe$_\alpha$In$_{1-\alpha}$) mixed-MOFs designed for enhancing photocatalytic Cr(VI) reduction and tetracycline elimination†

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Aiming at solving the issue of wastewater purification, this work synthesized NH$_2$-MIL-88B (Fe$_\alpha$In$_{1-\alpha}$) photocatalysts by a simple one-pot method, which was employed for photocatalytic reduction of Cr(VI) and oxidation of TC-HCl. Compared with traditional NH$_2$-MIL-88B (Fe) photocatalysts, NH$_2$-MIL-88B (Fe$_\alpha$In$_{1-\alpha}$) displayed excellent photocatalytic performance; the photocatalytic redox rate for Cr(VI) and TC-HCl reached 86.83% and 72.05%, respectively. The good photocatalytic performance might be attributed to the metal-to-metal charge transition (MMCT) between Fe–O clusters and In–O clusters formed by doping In(III) into NH$_2$-MIL-88B (Fe), which provides effective active sites for the photocatalytic reduction and oxidation routes. Besides, the synergistic effect of the ligand-to-metal charge transition (LMCT) and MMCT expands the separation and transfer of photogenerated carriers and inhibits the recombination of electron–hole pairs, thus effectively improving the photocatalytic performance. Therefore, this work could provide a new method for the construction of mixed metal MOFs for the photocatalytic degradation of pollutants.

Introduction

Heavy metals and residual antibiotics in wastewater have become a serious threat to living creatures and the environment.¹–⁴ Hexavalent chromium (Cr(VI)), as a heavy metal ion pollutant in wastewater with high toxicity and mobility, has seriously threatened human health and the natural environment.⁵,⁶ If a large amount of Cr(VI) existed in the drinking water system, it would cause damage to the human stomach, kidneys, liver, and retinas and also serious environmental concern.⁷–⁸ Therefore, it is urgent to remove Cr(VI) from wastewater. There are many existing solutions such as chemical precipitation,⁹ membrane separation,¹⁰ ion exchange,¹¹ activated carbon adsorption¹² and photocatalytic reduction.¹³–¹⁵ Among them, the reduction of Cr(VI) to Cr(III) by semiconductor photocatalysis is a very effective strategy due to the low toxicity of Cr(III).¹⁶–¹⁸ Furthermore, tetracycline hydrochloride (TC-HCl), as one of the most common antibiotics, is widely used in various industries such as medicine, agriculture, and animal husbandry. TC-HCl is abundant in the environment due to its stable chemical structure and non-biodegradation, which has already imperiled the ecosystem and human health.¹⁹–²¹ There are many current ways to remove TC-HCl, including adsorption,²² advanced oxidation processes (AOPs),²³ biological degradation,²⁴ electrolysis,²⁴ membrane filtration,²⁵ ion exchange²⁶ and photocatalytic degradation.²⁷,²⁸ Photocatalytic degradation is widely used in recent years because of mild reaction conditions, high efficiency, low cost and greenly.²⁹–³¹

Metal–organic frameworks (MOFs), as a class of crystalline inorganic–organic hybrid materials, are composed of the interconnection between metal centers and multidentate organic ligands.³²–³⁴ MOFs have been valued by researchers in the field of photocatalysis³⁵ due to the inherent large specific surface area, uniform and adjustable pore structure, and abundant active sites.³⁶ Under the irradiation of incident light, the photogenerated electrons are excited from the valence band (VB) and transferred to the conduction band (CB) through the ligand-to-metal charge transition (LMCT) process. The separated photogenerated electrons–holes pairs can perform the reduction and oxidation reaction with the reactants adsorbed on the catalyst surface.³⁷ Traditional MOFs existed some shortcomings, such as small photoresponse range and high electrons–holes recombination rate.³⁸ It is undoubtedly a good way to change the photoresponse range and photocatalytic performance of MOFs by adjusting the central metal or organic ligands.³⁹ The strategy of combining two or more transition metals into the same framework to form mixed-metal MOFs has aroused the interest of researchers.⁴⁰

Mixed-metal organic framework (MM-MOFs), containing two or more metal centers, are periodically arranged with a single ligand in the whole framework.⁴¹,⁴² There is a metal-to-metal
charge transition (MMCT) process between multiple metals in
MM-MOFs, which facilitates the transfer of photogenerated
electrons and inhibits the recombination of electrons–holes
pairs. Compared with single-metal MOFs, the synergistic
effects between LMCT and MMCT of MM-MOFs can effectively
improve the photocatalytic activity in various applications.8,9 Also,
MM-MOFs can effectively control the electronic structure and
bandgap structure while increasing the metal active sites.10,11 For
instance, Vu et al. synthesized Fe-Cr-MIL-101 for dye degradation
by the hydrothermal method. Mixed-metal MOFs showed better
adsorption capacity and higher photocatalytic activity and
stability in comparison with Cr-MIL-101.11 Maite P. et al. studied
the synthesis of multimetal MOFs doped with Zn(II), Ru(II) and
Pd(II) into Cu-MOF and applied to electrochemical reduction of
CO2.12 In our previous report, we successfully synthesized NH2-
MIL-88B (In1Fe1-C09H2O) that displayed good photocatalytic activity.13
According to reports, NH2-MIL-88B (Fe) has a flexible pore structure
and a large open structure channel due to its 3D porous
structure containing hexagonal channels and bipyramidal
cages.14 The wide and flexible pore structure facilitated other
metal ions to smoothly enter the 3D structure to replace the
original central metal ions, and can provide adjustment space for
structural changes that may be caused by the introduction of other
central metal ions, thereby improving related performance.

Based on the above analysis, a novel MM-MOFs material
NH2-MIL-88B (Fe1In15−a) was constructed and synthesized via
the one-pot method directly, which used NH2-MIL-88B (Fe) as
the structural framework. Under visible light irradiation, the
activity of photocatalytic treatment of pollutants in water was
tested. The results showed that the efficiency of Cr(Ⅵ) reduction
and TC-HCl oxidation of NH2-MIL-88B (Fe1In15−a) was 1.7 and
1.6 times that of NH2-MIL-88B (Fe). Moreover, a possible
photocatalytic mechanism was proposed through characterization
and performance and active species testing. This work provides
an effective way for the construction of MM-MOFs and the
photocatalytic degradation of various pollutants in wastewater.

Experimental sections

The chemicals and characterization details could be found in
ESI†

Synthesis of NH2-MIL-88B (Fe)

The NH2-MIL-88B (Fe) sample was prepared via a one-pot
method. 2-Aminoterephthalic acid (NH2-BDC) (0.54 mmol)
and Fe(NO3)3·9H2O (0.48 mmol) were dissolved in DMF
(12 mL), added CH3CN (12 mL) after mixed well. Then, and
the mixture was transferred into a flask, oil bath at 120 °C for
45 min. The suspension was cooled to room temperature
naturally and washed with methanol. The sample was dried at
70 °C for 5 h, then NH2-MIL-88B (Fe) was gained.

Synthesis of In-doped NH2-MIL-88B (Fe)

In-doped NH2-MIL-88B (Fe) was synthesized through the above
similar process, except that pure Fe(NO3)3·9H2O was replaced
with different ratios Fe(NO3)3·9H2O and In(NO3)3·xH2O. The
products were named as NH2-MIL-88B (FeIn15−a), and the
synthesis diagram was shown in Scheme 1.

Evaluation of photocatalytic performance

The photocatalytic performance of as-obtained samples was
evaluated by removing Cr(Ⅵ) and TC-HCl. A certain amount of
synthesized NH2-MIL-88B (Fe1In15−a) was added into the Cr(Ⅵ)
solution and stirring sufficiently. Simultaneously, the pH value of
the Cr(Ⅵ) solution was adjusted to 2 with HCl solution. Then
proceed to photocatalytic degradation. During the experiment,
pay attention to the concentration of Cr(Ⅵ) in the system. The
suspension was stirred for some time under dark conditions.
When the concentration of Cr(Ⅵ) no longer changed, switch to
Xe lamp irradiation. The suspensions taken out regularly are
centrifuged and filtered with a 0.22 μm syringe filter. The
determination was realized by the UV-visible spectrophotometer.

\[
\text{Efficiency} (\%) = \frac{C}{C_0} \times 100\%
\]

where \(C\) and \(C_0\) are the concentrations of pollutants in the water at \(t\) and \(t_0\).

Results and discussions

Structure and morphology analysis

As revealed in Fig. 1a, the crystalline structure of NH2-MIL-88B
(Fe) and In-doped NH2-MIL-88B (FeIn15−a) are confirmed by
the XRD pattern. The obvious characteristic peaks of NH2-MIL-
88B (Fe) located at 9.21°, 10.25°, 13.07°, 16.65°, 18.53°, 20.69°,
consistent with the literature reported,15 verified the successful
preparation of NH2-MIL-88B (Fe). The doped amounts of In on
NH2-MIL-88B (Fe) determined by the ICP-AES analysis as shown
in Table S1† Concomitantly, the main characteristic peaks of
NH2-MIL-88B (FeIn15−a) appeared in the same position as
NH2-MIL-88B, which preliminarily proved that NH2-MIL-88B
(FeIn15−a) was successfully prepared. The as-prepared MM-
MOFs mainly exist combination and crystal lattice in the form

Scheme 1 Synthesis diagram of the synthetic processes of NH2-MIL-
88B (FeIn15−a).
of NH2-MIL-88B (Fe). As the molar ratio of In(m) ions increases, the characteristic peak at 9.21° shifts to 9.02°. The deviation of the characteristic peak might be due to that the ion size of In(m) (94.0 pm) in the crystal structure was significantly larger than that of FeO6 octahedron, which was compared a new characteristic absorption peaks, the characteristic absorption spectrum, which corresponding to the C 1s, N 1s, In 3d, O 1s, Fe 2p electron orbitals, respectively. These elements in Fig. 3a. There are four characteristic peaks in the XPS spectrum shown in Fig. 3d. The peaks at 531.7 and 530.8 eV correspond to the characteristic peaks of In (Fe) and Fe elements were approved in the EDX images, which even demonstrated the conformation of MM-MOFs NH2-MIL-88B (Fe,In1−x).

**XPS analysis**

The XPS spectra of NH2-MIL-88B (Fe0.6In0.4) composite is shown in Fig. 3a. There are five characteristic peaks in the survey spectrum, which corresponding to the C 1s, N 1s, In 3d, O 1s, and Fe 2p electron orbitals, respectively. These elements confirm the results of the EDX analysis as displayed in Table S3.† Fig. 3b is the characteristic peak of C, all of them are derived from organic ligands. The characteristic peaks at 284.1, 286.2, and 288.2 eV could be attributed to C=–C, C–N and C=O respectively, which correspond to various carbon-containing covalent bonds in NH2-BDC.51 In Fig. 3c, the XPS spectrum of O 1s can be divided to 396.8 and 397.9 eV, which represents the –NH2 and –NH– respectively. It belonged to the amino group extending or protruding into the cavity and the positively charged. There are four characteristic peaks in the XPS spectrum of O 1s shown in Fig. 3d. The peaks at 531.7 and 530.8 eV can be attributed to –OH and C=O of the organic ligand. Also, 529.9 and 529.1 eV correspond to the characteristic peaks of In–O and Fe–O respectively. The appearance of In–O clusters shows that In(m) has been doped into the catalyst and connected to the organic ligands, thus successfully constructing NH2-MIL-88B (Fe,In1−x), which is consistent with the results of TEM. Fig. 3e shows the characteristic peaks of Fe 2p, where the satellite peak of Fe is at 715.2 eV. Among the peaks of Fe 2p1/2 and Fe 2p3/2, 724.0 eV and 710.0 eV represent Fe3+, and 722.2 eV and 709.0 eV represent Fe2+.54–56 The appearance of Fe2+ is due
has the strongest absorption intensity of visible light, and NH$_2$-MIL-88B (Fe$_{0.6}$In$_{0.4}$) has a slight enhance in visible light absorption intensity. Comparing with NH$_2$-MIL-88B (Fe), both have significantly enhanced visible light absorption. Thereby, this indicates that a certain proportion of In($\text{III}$) doping, which is beneficial to improve the visible light absorption capacity of NH$_2$-MIL-88B (Fe).

The corresponding bandgap energy ($E_g$) values could be calculated by following the eqn (1)

\[
(\alpha h\nu)^2 = A(h\nu - E_g)
\]

here, $\alpha$, $h$, $\nu$, $A$, $E_g$ corresponds to the absorption coefficient, the Planck’s constant, light frequency, constant, the bandgap energy, respectively. As displayed in Fig. 4b, the $E_g$ values of NH$_2$-MIL-88B (Fe), NH$_2$-MIL-88B (Fe$_{0.6}$In$_{0.4}$), NH$_2$-MIL-88B (Fe$_{0.4}$In$_{0.6}$), NH$_2$-MIL-88B (Fe$_{0.1}$In$_{0.9}$) and NH$_2$-MIL-88B (Fe$_{0}$In$_{1.0}$) were estimated to be 2.62, 2.48, 2.58, 2.66 and 2.69 eV, respectively. The size of the bandgap energy is related to the difficulty of electronic excitation. Under visible light irradiation, the lower bandgap energy can allow more electrons to excite the transition to CB, promote the effective separation of electrons and holes, thereby improving the photocatalytic activity. Among them, NH$_2$-MIL-88B (Fe$_{0.4}$In$_{0.6}$) and NH$_2$-MIL-88B (Fe$_{0}$In$_{1.0}$) displayed the lower $E_g$ and the stronger visible light response-ability, which may perform better photocatalytic performance.

As shown in Fig. S1,$^\dagger$ the fluorescence intensity of NH$_2$-MIL-88B (Fe$_{0.6}$In$_{0.4}$) is significantly lower than that of NH$_2$-MIL-88B (Fe), which indicates that the addition of In($\text{III}$) inhibits the recombination of photogenerated e$^-$–h$^+$, thereby allowing more photogenerated carriers to participate photocatalytic reaction.$^{57,58}$

**Photocatalytic activities**

For verifying the photocatalytic performance of NH$_2$-MIL-88B (Fe$_{0.4}$In$_{0.6}$) obtained from the characterization results, we conducted experiments on photocatalytic Cr(VI) reduction under different catalytic conditions. As displayed in Fig. 5a, the Cr(VI) concentration was unaltered significantly with visible light irradiation and no photocatalyst, at the same time, the small range change of Cr(VI) concentration was due to adsorption with photocatalyst and no light, which indicated that visible light irradiation played an important role in the photocatalytic reduction of Cr(VI). The photocatalytic reduction efficiency of NH$_2$-MIL-88B (Fe$_{0.6}$In$_{0.4}$) for reducing Cr(VI) is 86.83%, which is significantly higher 1.7 times than that of NH$_2$-MIL-88B (Fe) of 50.96%, thereby, which demonstrated that the doping of In($\text{III}$) effectively improves the photocatalytic reduction performance. As shown in Fig. 5b, the different In($\text{III}$) doped amount of NH$_2$-MIL-88B (Fe$_{0.4}$In$_{0.6}$) was carried out to discuss the capability of photocatalytic Cr(VI) reduction. With the doping of In($\text{III}$), the photocatalytic reduction effect of the catalyst gradually increases. Among them, NH$_2$-MIL-88B (Fe$_{0.4}$In$_{0.6}$) has the highest photocatalytic reduction rate. By contrast, NH$_2$-MIL-88B (Fe$_{0}$In$_{1.0}$) is the lowest one. With the addition of more In($\text{III}$) content, the catalytic effect gradually decreases. This may be due to more In($\text{III}$) doping, resulting in lower visible light absorption. And higher bandgap energy is not conducive to the
excitation of electrons on VB, thereby reducing the photocatalytic activity of photocatalytic reduction of hexavalent chromium. Meanwhile, Fig. 5c shows that the photocatalytic Cr(VI) on different concentrations reduction performance of NH2-MIL-88B (Fe0.6In0.4) was investigated. With increasing the amount of catalyst, the photocatalytic performance gradually increases, reaching the maximum at 10 mg L\(^{-1}\). However, an excess of the catalyst leads to lower photocatalytic reduction efficiency. This may be due to excessive catalyst hindering the light irradiation of the Cr(VI) solution. Fig. 5d displays that the photocatalytic reduction efficiency has a good linear relationship with the reaction time, which conforms to the first-order reaction kinetics. The pseudo-first-order rate constant \(k\) is obtained by the following formula:

\[
\ln(C_0/C) = kt
\]

here, \(C_0\), \(C\), \(k\), and \(t\) corresponds to the initial concentrations of Cr(VI), the concentrations of Cr(VI), the pseudo-first-order rate constant, and time, respectively. The value of \(k\) and \(R^2\) of NH2-MIL-88B (Fe) and NH2-MIL-88B (Fe0.6In0.4) was displayed in Tables S4 and S5.†

To investigate the oxidation performance of the prepared photocatalyst, the photocatalytic degradation of TC-HCl by NH2-MIL-88B (Fe0.6In1.0) under different catalytic conditions was performed. Similar to the photocatalytic reduction effect of Cr(VI), the test result of Fig. 6a shows that the light and photocatalyst are crucial in the reaction system. As shown in Fig. 6b, the photocatalytic degradation efficiency of NH2-MIL-88B (Fe0.6In1.0) on TC-HCl under visible light irradiation conditions is 72.05%, which is significantly higher 1.6 times than that of NH2-MIL-88B (Fe) of 44.68%. Fig. 6c demonstrated the effect of different concentrations photocatalytic degradation efficiency of TC-HCl. Among them, as the content of TC-HCl increases, the degradation rate gradually decreases, and when the content is 10 mg, NH2-MIL-88B (Fe0.6In1.0) displays the best degradation effect. The relationship between \(\ln(C_0/C)\) and time shows that the photocatalytic degradation efficiency has a good linear relationship with the reaction time, as presented in Fig. 6d, which is in line with the first-order reaction kinetics. The value of \(k\) and \(R^2\) of NH2-MIL-88B (Fe) and NH2-MIL-88B (Fe0.6In1.0) was displayed in Tables S6 and S7.†

To detect the reactive oxygen species generation during the photocatalytic degradation of TC-HCl by NH2-MIL-88B (Fe0.6In1.0), electron spin resonance (ESR) technique is employed. Fig. 7 depicts the conspicuous characteristic peak signals of DMPO-\(\cdot\)O\(_2\)\(^{-}\) and DMPO-\(\cdot\)OH, which confirms the generation of \(\cdot\)O\(_2\) and \(\cdot\)OH radicals in the experiment. The peak intensity ratio of the quadruple characteristic peak signal of DMPO-\(\cdot\)OH is about 1 : 2 : 2 : 1.\(^{39}\) NH2-MIL-88B (Fe0.6In1.0) by the photocatalyst generates \(\cdot\)OH under visible light irradiation, which can activate dissolved oxygen in the solution that promotes oxygen molecules to become `O\(_2\)` species and can

\[
\text{EPR spectra of DMPO-}\cdot\text{O}_2^\cdot \text{ and DMPO-}\cdot\text{OH adducts generated by NH}_2\text{-MIL-88B (Fe)}_{0.6}\text{In}_{1.0}\text{ after 60 seconds under visible light irradiation (}\lambda > 400\text{ nm) during the photocatalytic process.}
\]
also interact with water molecules to generate ‘OH species, simultaneously.

**Mechanism**

Based on the above results, the possible mechanism of NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$) photocatalytic treatment of Cr(vi) and TC-HCl in water is proposed. First, the electrons transfer process of NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$) photocatalytic reduction of Cr(vi) is as follows. Under visible light irradiation, the organic ligand of NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$) can be excited to generate electrons and holes. A part of the photogenerated electrons transfers to the surface of the catalyst through the In–O clusters through the LMCT to reduce Cr(VI) adsorbed directly. Then, the In–O clusters transfer another electron to the Fe–O cluster through MMCT, which promotes the separation of electrons and holes effectively.

The excitation and transfer of photogenerated carriers of photocatalytic oxidation of TC-HCl are similar to the process of reduction of Cr(vi). The photogenerated electrons transfer to the surface of the catalyst combine with O$_2$ and H$_2$O in the solution to produce ‘O$_2$’ and ‘OH. Both the holes generated by NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$) excited by visible light and ‘O$_2$’/‘OH can interact with TC-HCl directly and eventually generate CO$_2$ and H$_2$O. Anyway, the MMCT in the NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$) expands the active sites of photocatalytic oxidation-reduction. Also, the synergistic process of LMCT and MMCT effectively inhibits the recombination of electrons and holes, thereby enhancing the performance of the NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$) (Scheme 2).

**Conclusions**

In summary, a series of NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$) photocatalysts were designed and synthesized via a one-pot method. Proved by characterizations of TEM and XPS, In(III) ions successfully replaced part of Fe(III) ions in the structure, which formed mixed-metal MOFs NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$). Compared with single NH$_2$-MIL-88B (Fe), NH$_2$-MIL-88B (Fe$_{0.6}$In$_{0.4}$) shows excellent photocatalytic performance: the reduction rate of Cr(VI) and the oxidation rate of TC-HCl reach 86.83% and 72.05%, which 1.7 and 1.6 times that of NH$_2$-MIL-88B (Fe), respectively. The improvement of photocatalytic performance is mainly attributed to the more reactive sites when In(III) doped to NH$_2$-MIL-88B (Fe). Simultaneously, the synergistic effect of LMCT and MMCT of NH$_2$-MIL-88B (Fe$_{1-x}$In$_x$) effectively expands the separation and transfer of photogenerated carriers and inhibits the recombination of electrons–holes pairs, thereby enhancing the performance of photocatalytic reduction of Cr(vi) and oxidative degradation of TC-HCl. This work may provide an insight to design and develop mixed-metal MOFs as photocatalysts for the wastewater treatment.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

Thanks to the 2020 School-level Scientific Research Project of Dalian Vocational & Technical College (Dalian Radio and TV University) and the Key Project of Natural Science Foundation of Liaoning Province (No. 20170540578).

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