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Article

Enhanced photocatalytic Cr(VI) reduction and diclofenac sodium degradation under simulated sunlight irradiation over MIL-100(Fe)/g-C₃N₄ heterojunctions

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ABSTRACT

Metal-organic framework MIL-100(Fe) and g-C₃N₄ heterojunctions (MG-*x*, *x* = 5%, 10%, 20%, and 30%, *x* is the mass fraction of MIL-100(Fe) in the hybrids) were facilely fabricated through ball-milling and annealing, and characterized by powder X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, transmission electron microscopy, UV-visible diffuse-reflectance spectrometry, and photoluminescence emission spectrometry. The photocatalytic activities of the series of MG-*x* heterojunctions toward Cr(VI) reduction and diclofenac sodium degradation were tested upon irradiation with simulated sunlight. The influence of different organic compounds (ethanol, citric acid, oxalic acid, and diclofenac sodium) as hole scavengers and the pH values (2, 3, 4, 6, and 8) on the photocatalytic activities of the series of MG-*x* heterojunctions was investigated. MG-20% showed superior photocatalytic Cr(VI) reduction and diclofenac sodium degradation performance than did the individual MIL-100(Fe) and g-C₃N₄ because of the improved separation of photoinduced electron-hole charges, which was clarified via photoluminescence emission and electrochemical data. Moreover, the MG-*x* exhibited good reusability and stability after several runs.

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1. Introduction

Among toxic heavy metal ions, hexavalent chromium (Cr(VI)) is a mutagenic and carcinogenic contaminant that is found in surface water and groundwater, as it is widely utilized

in the electroplating, leather tanning, printing, polishing, and pigment industries [1–3]. Up to now, photocatalytic reduction of Cr(VI) to Cr(III) has been a hot topic of research [4–10], therefore, it is a great challenge to develop novel photocatalysts with efficient visible-light absorption and excellent stability

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[8,11]. Among the various photocatalysts, graphitic carbon nitride (g-C₃N₄) is a good, metal-free photocatalyst that possesses appealing features like π -conjugated electronic structure, high chemical stability, and earth abundance [12,13]. However, g-C₃N₄ has some disadvantages, such as high recombination probability of the photogenerated electron-hole pairs due to hybridization of the N 2*p* and C 2*p* states in the conduction band (CB) and unavoidably disordered structure or defects [14–16] and low surface area resulting from the bulk structure [17–19]. These disadvantages lead to the low photocatalytic activity for Cr(VI) reduction or organic pollutant degradation. Recently, synthesis of g-C₃N₄ composites with different materials, such as g-C₃N₄/Bi₂WO₆ [20], g-C₃N₄/SiW₁₁ [21], g-C₃N₄/Zn₃V₂O₇(OH)₂(H₂O)₂ [22], WO₃/g-C₃N₄ [23], g-C₃N₄/Ag₂O [24], and g-PAN/g-C₃N₄ [25], has been identified to be an efficient way to improve the photocatalytic reduction efficiency.

Recently, the application of metal-organic frameworks (MOFs) in heterogeneous photocatalysis under UV/visible/UV-vis irradiation for water splitting and CO₂ & Cr(VI) reduction by using photogenerated electrons as well as the degradation of organic pollutants based on holes has become widespread [8,26–30]. The photocatalytic performance of composites containing g-C₃N₄ and MOFs has been widely reported. For example, ZIF-9(Co)/g-C₃N₄ exhibited multiple functions in both CO₂ adsorption and high photocatalytic activity for CO₂ reduction [31]. UiO-66(Zr)/g-C₃N₄ demonstrated efficient photocatalytic hydrogen production because of the heterojunctions [32]. MIL-125(Ti)/g-C₃N₄, MIL-53(Al)/g-C₃N₄, and MIL-100(Fe)/g-C₃N₄ exhibited highly efficient photocatalytic performance toward rhodamine B degradation in aqueous solution under visible-light irradiation [12,33,34]. ZIF-8(Zn)/g-C₃N₄ is a bifunctional material that shows efficient adsorption and facilitates sunlight-induced photocatalytic degradation of tetracycline [35]. ZIF-NC/g-C₃N₄ composites exhibit enhanced photocatalytic activity for bisphenol A degradation with peroxymonosulfate under visible-light irradiation [36]. Moreover, MIL-53(Fe)/g-C₃N₄ had improved photocatalytic efficiency for Cr(VI) reduction [37].

In this work, MIL-100(Fe)/g-C₃N₄ hybrids were synthesized through ball-milling and annealing for photocatalytic Cr(VI) reduction under different conditions. Both g-C₃N₄ and MIL-100(Fe) showed photocatalytic performance, but each material when used individually exhibited limited photocatalytic efficiency due to the high charge recombination rate and limited light absorption ability. The MIL-100(Fe)/g-C₃N₄ hybrids obtained by combining MIL-100(Fe) with g-C₃N₄ demonstrated outstanding photocatalytic performance for Cr(VI) reduction under simulated sunlight, along with good stability and reusability.

2. Experimental

2.1. Materials

All chemicals including urea (CH₄N₂O, USP grade, Amresco), iron powder (Fe, 99%, J&k Scientific Ltd.), ben-

zene-1,3,5-tricarboxylic acid (H₃BTC, C₉H₆O₆, 99%, J&k Scientific Ltd.), nitric acid (HNO₃, analytical grade, Sinopharm Chemical Reagent Co., Ltd.), hydrofluoric acid (HF, analytical grade, Sinopharm Chemical Reagent Co., Ltd.), potassium dichromate (K₂Cr₂O₇, analytical grade, Sinopharm Chemical Reagent Co., Ltd.), diclofenac sodium (C₁₄H₁₀Cl₂NNaO₂, 98%, J&k Scientific Ltd.), hydrogen peroxide (H₂O₂, 30 wt%, Sinopharm Chemical Reagent Co., Ltd.), oxalic acid (H₂C₂O₄, analytical grade, Sinopharm Chemical Reagent Co., Ltd.), citric acid monohydrate (C₆H₈O₇·H₂O, 99%, J&k Scientific Ltd.), sodium acetate (C₂H₃O₂Na, analytical grade, Sinopharm Chemical Reagent Co., Ltd.), and acetonitrile (C₂H₃N·H₂O, LC-MS grade, J&k Scientific Ltd.) were commercially available and used without further purification.

2.2. Preparation of MIL-100(Fe)/g-C₃N₄ hybrids

g-C₃N₄ was prepared by calcination with urea as the precursor [33]. Briefly, 10.0 g of urea was placed in a porcelain crucible with a cover, moved into a muffle furnace, and heated at 500 °C for 4 h. The obtained yellow powder was collected for further use. Crude g-C₃N₄ powder (1.0 g) was dispersed in 200.0 mL deionized H₂O by sonication for 6 h. Then, pure g-C₃N₄ was obtained by centrifuging the supernatant at 6000 rpm for 10 min and dried at 60 °C for 6 h.

MIL-100(Fe) was synthesized according to the procedure reported by Horcajada and coworkers [38]. A mixture of 0.139 g Fe⁰, 0.344 g H₃BTC, 0.1 mL HF, 0.1 mL HNO₃, and 10.0 mL H₂O with a molar ratio of 1.0:0.66:2.0:1.2:280 was sealed in a 25.0 mL Teflon-lined autoclave and heated at 150 °C for 6 d. The light-orange MIL-100(Fe) was collected by filtration, washed with deionized water, and finally dried in an oven at 60 °C for 2 h.

The MIL-100(Fe)/g-C₃N₄ heterojunctions (MG-*x*, *x* = 5%, 10%, 20%, and 30%, *x* is the mass fraction of MIL-100 in hybrids) were fabricated by ball-milling, followed by thermal treatment of the mixture of g-C₃N₄ and MIL-100(Fe). In a typical procedure, a certain amount of MIL-100(Fe) and g-C₃N₄ powders was mixed in a stainless-steel pot and ground for 20 min using a ball mill. The ground mixture was then thermally treated at 300 °C for 2 h in a tube furnace under N₂ atmosphere to produce a series of MIL-100(Fe)/g-C₃N₄ (MG-*x*) heterojunctions. For comparison, pristine g-C₃N₄ and MIL-100(Fe) were also thermally treated under the same conditions as those for the MG-*x* hybrids.

2.3. Characterization

Powder X-ray diffraction (PXRD) patterns of the samples were obtained with a Dandong Haoyuan DX-2700B diffractometer in the range of $2\theta = 5^\circ$ – 50° with Cu K α radiation. Thermogravimetric analyses (TGA) were performed in the range of 90–800 °C in an air stream at a heating rate of 10 °C/min on a DTU-3c thermal analyzer using α -Al₂O₃ as a reference. Fourier transform infrared (FT-IR) spectra were recorded using KBr pellets on a Nicolet 6700 spectrometer in the range of 4000–400 cm^{−1}. UV-visible diffuse-reflectance spectra (UV-vis

DRS) of the solid samples were measured in the range of 200–800 nm on a Perkin Elmer Lambda 650S spectrophotometer, in which barium sulfate (BaSO_4) was used as the standard with 100% reflectance. Photoluminescence (PL) emission spectra were recorded on a Hitachi F-7000 spectrophotometer across wavelengths ranging from 400 to 600 nm at room temperature, with an excitation wavelength of 320 nm. The surface area of the sample was calculated from N_2 adsorption-desorption isotherms measured on a BELSORP-mini II surface area analyzer at -196°C using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method. The morphology of the samples was observed using a Hitachi HT7700 transmission electron microscope (TEM) operating at an acceleration voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with Thermo ESCALAB 250XI.

2.4. Electrochemical measurements

Electrochemical measurements were conducted using a Metrohm Autolab PGSTAT204 electrochemical station in a typical three-electrode mode with 0.2 mol/L Na_2SO_4 aqueous solution ($\text{pH} = 6.8$) as the electrolyte. A Pt electrode and a saturated Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. Powder samples of 5.0 mg MIL-100(Fe) or $\text{g-C}_3\text{N}_4$ were mixed sufficiently with 400.0 μL ethanol/Nafion ($v/v = 19/1$) under sonication for 30 min to prepare the working electrodes. The prepared slurry (10.0 μL) was drop-cast onto the conductive side of a Fluorine-doped Tin Oxide (FTO) substrate ($1.0\text{ cm} \times 1.0\text{ cm}$), and then dried at 80°C for 30 min. This step was repeated five times to ensure uniform coverage of MIL-100(Fe) or $\text{g-C}_3\text{N}_4$ on the FTO substrate for obtaining the desired working electrodes.

2.5. Photocatalytic experiment

The photocatalytic Cr(VI) reduction experiment was carried out at 25°C in a 300 mL quartz reactor containing 100.0 mg of the photocatalyst and 200.0 mL of 10.0 ppm Cr(VI) aqueous solution, and the solution pH was adjusted to 2.0–8.0 with 0.2 mol/L H_2SO_4 or 0.2 mol/L NaOH solution. After stirring for 60 min to achieve adsorption-desorption equilibrium, the suspensions were irradiated by a 300 W xenon lamp (Beijing Aulight Co., Ltd.). The spectrum of the light source is shown in Fig. S1 (Supporting Information). During illumination, 2.5 mL of the suspension was taken from the reactor at specific time intervals and centrifuged to separate the photocatalyst. The Cr(VI) content in the supernatant was determined colorimetrically at 540 nm using the diphenylcarbazide method with a Yuanxi UV-5200PC UV-vis spectrophotometer [39].

The photocatalytic degradation performance of the MG- x nanocomposites toward diclofenac sodium was also tested. In a typical experiment, 100.0 mg of photocatalyst powder was dispersed in 200.0 mL diclofenac sodium aqueous solution (0.1 mmol/L). The suspension was stirred in the dark for 60 min to achieve adsorption-desorption equilibrium, and then, hydrogen peroxide (50.0 μL) was added to the suspension before

turning on the light. A 300 W xenon lamp (Beijing Aulight Co. Ltd.) was used as the light source. During the photocatalytic degradation, the samples were collected at regular time intervals using a 0.22-mm syringe filter to remove the photocatalyst particles before analysis. An Acquity UPLC H-Class (Waters) system was used to detect the residual concentration of diclofenac sodium after the photocatalytic degradation. The analytes were separated on a C18 ($1.7\text{ }\mu\text{m}$, $2.1\text{ mm} \times 50\text{ mm}$) column in a UPLC system equipped with a TUV detector. Aqueous sodium acetate solution (0.015 mol/L) and acetonitrile were used as mobile phases A and B, respectively. The gradient was programmed as follows: 0–0.5 min, 0–0% B; 0.5–1 min, 0–48% B; 1–2 min, 48–48% B; 2–2.5 min, 48–0% B. The column temperature was maintained at 40°C .

3. Results and discussion

3.1. Characterization

The PXRD patterns of the parent materials and heterojunctions are illustrated in Fig. 1. The PXRD patterns of MIL-100(Fe) were consistent with those reported in the literature (Fig. S2) [38,40], demonstrating that the prepared MIL-100(Fe) was pure and well crystallized. The typical interlayer-stacking peak (002) at $2\theta = 27.2^\circ$ corresponded to an interlayer distance of $\sim 0.32\text{ nm}$ for $\text{g-C}_3\text{N}_4$ [41,42]. The PXRD patterns of the MG- x composites matched well with the corresponding peaks of $\text{g-C}_3\text{N}_4$ and MIL-100(Fe), implying their successful combination. More importantly, no sign of a new phase in the MG- x hybrids was observed after annealing; the characteristic peaks at 6.2° , 10.2° , 11.0° , and 20.0° attributed to MIL-100(Fe) became more evident with increasing mass content in the MG- x samples. The unchanged backbones of $\text{g-C}_3\text{N}_4$ and MIL-100(Fe) in the MG- x hybrids were further revealed by the identical FTIR spectra, as shown in Fig. 2. As expected, the same characteristic absorption peaks were observed for $\text{g-C}_3\text{N}_4$ and MG- x hybrids, except for the low MIL-100(Fe) content in the MG- x samples. The texture of MG-20% hybrids was selected for observation in the TEM and HRTEM images, as shown in

Fig. 1. XRD patterns of $\text{g-C}_3\text{N}_4$, MG- x ($x = 5\%$, 10% , 20% , and 30%) hybrids, and MIL-100(Fe).

Fig. 2. FTIR spectra of g-C₃N₄, MG-*x* (*x* = 5%, 10%, 20%, and 30%) hybrids, and MIL-100(Fe).

Fig. 3. TEM images of (a) pure MIL-100(Fe), (b) pure g-C₃N₄, and (c) MG-20%, and (d) HRTEM image of MG-20%.

Fig. 3. For comparison, the TEM images of pure MIL-100(Fe) and g-C₃N₄ were also included. MIL-100(Fe) (Fig. 3(a)) displayed a polygonal structure [34], and g-C₃N₄ samples (Fig. 3(b)) exhibited aggregated, slate-like, and smooth particles with lamellar structures [33]. It could also be clearly observed that the g-C₃N₄ nanosheets adhered strongly to the edges of MIL-100(Fe) (Fig. 3(c)). High-resolution TEM images (Fig. 3(d)) could not be obtained as g-C₃N₄ and MIL-100(Fe) were solids with low crystalline quality [32]. TGA revealed that the thermal stability of MG-*x* decreased with an increase in the MIL-100(Fe) content in the MG sample, as shown in Fig. 4, and the residual weight further confirmed the different MIL-100(Fe) contents in the MG-*x* samples.

Fig. 5 presents the XPS survey spectrum and the high-resolution XPS spectra of MG-20%. The XPS survey spec-

Fig. 4. Thermal analysis of g-C₃N₄, MG-*x* (*x* = 5%, 10%, 20%, and 30%) hybrids, and MIL-100(Fe).

trum (Fig. 5(a)) shows that C, N, O, and Fe exist in MG-20%. Fig. 5(b) shows the C 1s XPS spectrum of MG-20%, in which the peaks at 284.3 eV/288.2 eV and 285.3 eV can be attributed to the *sp*²-bonded carbon (C–C bond)/C–H bond and C–N present in the g-C₃N₄, respectively [33,37], while the peaks at 284.9 and 288.7 eV can be ascribed to benzoic rings and C=O bonds of the H₂bdc ligand in MIL-100(Fe) [43]. Four binding energies in the N 1s region (Fig. 5(c)) can be observed, which can be ascribed to the C–N–C (398.7 eV), N–(C)₃ (400.1 eV), and N–H groups (401.3 eV), and the charging effects (404.9 eV), respectively [44]. The spectrum of MG-20% (Fig. 5(d)) exhibits two O 1s peaks at 531.2 and 532.2 eV, which are related to the Fe–O bonds of MG-20% and the oxygen components of the H₂bdc ligand, respectively [45]. Furthermore, the Fe 2p spectrum in Fig. 5(e) has two peaks at 712.5 and 725.4 eV, which can be assigned to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively [46]. These results clearly imply that the MG-20% photocatalyst is successfully fabricated. The UV-vis DRS spectra of g-C₃N₄, MIL-100(Fe), and MG-*x* are shown in Fig. 6(a). The band-gap energy (*E_g*) and band-edge wavelength (*λ_g*) of g-C₃N₄, MIL-100(Fe), and MG-*x* can be estimated using Eqs. (1) and (2), respectively [47].

$$Ah\nu = k(h\nu - E_g)^{1/n} \quad (1)$$

$$\lambda_g = 1240/E_g \quad (2)$$

where *k* represents a constant, and *n* is determined by the type of optical transition of a semiconductor. The results reveal that the *E_g* values of g-C₃N₄, MG-5%, MG-10%, MG-20%, MG-30%, and MIL-100(Fe) are 2.96, 2.87, 2.83, 2.80, 2.77, and 2.63 eV, respectively, and the band gaps tend to become narrow with an increase in the MIL-100(Fe) content. The PL spectra of g-C₃N₄ and MG-20% at an excitation wavelength of 320 nm are demonstrated in Fig. 7. The PL intensity of MG-20% at the 440 nm peak is weaker than that of pure g-C₃N₄, implying that the recombination rate of photogenerated electrons and holes decreases in case of MG-20% [48,49].

3.2. Photocatalytic activity

Before the photocatalytic reduction experiments, the adsorption abilities of the samples were tested. As shown in Fig. 8(a), the adsorption capacity of g-C₃N₄ and MG-*x* hybrids to-

Fig. 5. XPS spectra of the MG-20% hybrid. (a) Survey scan; (b) C 1s; (c) N 1s; (d) O 1s; (e) Fe 2p.

Fig. 6. (a) UV-vis spectra and (b) $(Ah\nu)^2$ versus photon energy ($h\nu$) plots for g-C₃N₄, MG- x ($x = 5\%$, 10% , 20% , and 30%) hybrids, and MIL-100(Fe).

ward Cr₂O₇²⁻ was about 5%, while MIL-100(Fe) showed higher adsorption activity toward Cr₂O₇²⁻ (~20%) because of its positive surface at pH 2.0 [50,51]. The photocatalytic Cr(VI) reduction performance over MG- x ($x = 5\%$, 10% , 20% , and 30%) under simulated sunlight irradiation was evaluated, as illustrated in Fig. 8(a). All MG- x hybrids exhibited higher photocatalytic activities than those of pure g-C₃N₄ and MIL-100(Fe) owing to the synergistic effect between g-C₃N₄ and MIL-100(Fe). The MG-20% hybrid demonstrated the best photocatalytic activity, evidenced by its Cr(VI) reduction (97%) efficiency within 80 min. The kinetic curves for the photocatalytic reduction of Cr(VI) over MG- x (5%, 10%, 20%, and 30%) photocatalysts were plotted to the pseudo-first order model ($\ln(C/C_0) = kt$), and the values of k are shown in Fig. 8(b). The order of the Cr(VI) reduction rates for the as-prepared photocatalysts is as follows: MG-20% (0.037 min⁻¹) > MG-10% (0.028 min⁻¹) > MG-30% (0.026 min⁻¹) > MG-5% (0.023 min⁻¹) >

g-C₃N₄ (0.016 min⁻¹) > MIL-100(Fe) (0.012 min⁻¹). Appropriate introduction of MIL-100(Fe) into g-C₃N₄ will not only be beneficial for charge transfer at the heterojunction interfaces, but also improve visible-light harvesting (Fig. 6(a)). However, excess g-C₃N₄ may decrease the quality of effective heterointerfaces in MG- x , which would be unfavorable for charge transfer at the heterointerfaces [32,33,52].

During the redox process, the Cr(VI) reduction rate over the photocatalyst is greatly influenced by the pH of the aqueous solution. The reduction efficiencies of Cr(VI) over MG-20% at different pH values are shown in Fig. 9(a). The reduction ratio decreased rapidly with increasing pH (98%, 79%, 29%, 15%, and 9% at pH 2, 3, 4, 6, and 8, respectively). Under acidic conditions, the photocatalytic Cr(VI) reaction follows Eq. (4), and the abundant H⁺ further facilitates the conformation change from Cr(VI) to Cr(III) [8]. However, under alkaline conditions, CrO₄²⁻ is predominant, leading to a reaction as expressed in Eq. (6) [8].

Fig. 7. Photoluminescence spectra of g-C₃N₄ and MG-*x* (*x* = 5%, 10%, 20%, and 30%) hybrids.

Fig. 8. (a) Cr(VI) reduction photocatalytic performance of MIL-100(Fe), g-C₃N₄, and MG-*x* (*x* = 5%, 10%, 20%, and 30%) hybrids; (b) Rate constant k of MIL-100(Fe), g-C₃N₄, and MG-*x* hybrids. For comparison, the photocatalytic performance in a reaction without the catalyst is also given.

Moreover, the Cr(OH)₃ precipitate formed at pH > 6 covers the active sites of MG-20%, leading to a decline in its photocatalytic activity [52].

The consumption of holes (h^+) will accelerate photoinduced electron-hole charge separation and result in achieve out-

Fig. 9. Photocatalytic activities of the MG-20% hybrid for the reduction of Cr(VI) in aqueous solution at (a) different pH values and (b) different ethanol concentrations.

standing Cr(VI) reduction efficiency. To investigate the effect of some organic compounds as hole scavengers on the reduction efficiency, a series of experiments were carried out with the addition of different organic compounds like citric acid, oxalic acid, and diclofenac sodium at pH 2.0. As shown in Fig. 10(a), the addition of hole scavengers (citric acid and oxalic acid) increases the photocatalytic Cr(VI) reduction activity of MG-20%, which might be ascribed to the fact that citric acid and oxalic acid can consume the photoinduced holes produced by the MG-20% photocatalyst upon light irradiation (Eq. (5)) [53]. Thus, more electrons can escape from the pair recombination and become available for the reduction of Cr(VI) under acidic conditions. Ethanol can also capture photoinduced holes, and it was found that an increase in ethanol concentration led to faster Cr(VI) reduction, as shown in Fig. 9(b). However, the addition of diclofenac sodium does not increase the reduction efficiency, as it consumes the hydroxyl radicals, and not photoinduced holes.

To investigate the possible mechanism of the photocatalytic Cr(VI) reduction over MG-20%, the conduction bands (CBs) of MIL-100(Fe) and g-C₃N₄ were determined to be -0.11 and -1.12 V at pH 7.0 (Fig. 11(a) and (b)), respectively, by Mott-Schottky experiments. From the UV-Vis DRS spectra, the band gaps of MIL-100(Fe) and g-C₃N₄ were calculated to be 2.63 and 2.96 eV, respectively. Based on these values, the band structures of MIL-100(Fe) and g-C₃N₄ were determined, and a schematic diagram is shown in Fig. 12. Electron-hole pairs can be produced both on MIL-100(Fe) and g-C₃N₄. Fig. 12 illustrates

Fig. 10. (a) Photocatalytic activities of the MG-20% hybrid for the reduction of Cr(VI) in the presence of various hole scavengers; (b) Photocatalytic degradation of diclofenac sodium under different control conditions.

Fig. 11. Mott-Schottky plots of (a) MIL-100(Fe) and (b) $g-C_3N_4$ in 0.2 mol/L aqueous Na_2SO_4 solution (pH 7.0).

the charge carrier path in the MG-20% system. The photoexcited electrons from the CB of $g-C_3N_4$ move to the CB of MIL-100(Fe), which can suppress the recombination of photo-generated electron-hole pairs so that more free electrons are gathered in the CB of MIL-100(Fe). Consequently, MG-20% exhibits enhanced photocatalytic activity for Cr(VI) reduction

under simulated sunlight irradiation. To further evaluate the photocatalytic performance of the heterojunction structure, the MG-20% was tested for the degradation of diclofenac sodium under different conditions. In the absence of H_2O_2 , only 65.4% diclofenac sodium was degraded within 2 h, while 100% degradation was achieved within 50 min after adding H_2O_2 , as shown in Fig. 10(b). The above process can be summarized in Eq. (3) and Eqs. (7)–(8) as a Fenton-like reaction occurs [54,55].

To assess the practical application potential of the photocatalysts, the reusability and stability of MG-20% were also investigated. MG-20% was stable after a long-term stability test in an aqueous solution with pH 2.0, for up to 72 h. As shown in Fig. 13(a), the photocatalytic reduction efficiency of MG-20% does not obviously decrease after five runs of Cr(VI) reduction, indicating that the photocatalyst is highly stable and can be used for repeated treatment of Cr(VI). Moreover, the XRD patterns (Fig. 13(b)) of MG-20% before and after the photocatalytic reaction indicated that the crystal structure of MG-20% was not destroyed even after five cycles of the reaction. It can be concluded that MG-20% is stable during the photocatalytic process.

Fig. 12. Possible mechanism of photocatalytic reduction of Cr(VI) and degradation of diclofenac sodium over MG-20%.

Fig. 13. (a) Reusability of MG-20% in the reduction of Cr(VI); (b) XRD patterns of MG-20% before and after the photocatalytic reaction.

4. Conclusions

The facile fabrication of a series of photocatalytically active MIL-100(Fe)/g-C₃N₄ (MG-*x*) hybrids was accomplished. The optimal MG-20% hybrid demonstrated excellent photocatalytic activity for Cr(VI) reduction and organic pollutant degradation under simulated sunlight irradiation, which was superior to that of pure MIL-100(Fe) and g-C₃N₄. The results of electrochemical measurements and PL emission revealed that the enhanced Cr(VI) reduction was due to the efficient interfacial charge transfer from the photoexcited g-C₃N₄ to MIL-100(Fe). The different hole scavengers and pH value of the reaction solution played important roles in the photocatalytic Cr(VI) reduction. In the photocatalytic system, the addition of ethanol, citric acid, or oxalic acid facilitated the photocatalytic Cr(VI) reduction as the photogenerated holes were easily consumed.

Cyclic experiments also indicated the reusability and stability of MG-*x* for the photocatalytic Cr(VI) reduction. This work further demonstrates the great potential application of versatile MOFs and economic g-C₃N₄ for the development of active hetero-structured photocatalysts for environmental remediation.

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Graphical Abstract

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Enhanced photocatalytic Cr(VI) reduction and diclofenac sodium degradation under simulated sunlight irradiation over MIL-100(Fe)/g-C₃N₄ heterojunctions

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The MIL-100(Fe)/g-C₃N₄ hybrids show high photocatalytic activity under simulated sunlight and can reduce Cr(VI) to Cr(III) and decompose diclofenac sodium effectively.

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模拟太阳光照射下MIL-100(Fe)/g-C₃N₄异质结光催化Cr(VI)还原和双氯芬酸钠降解

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摘要: 有毒重金属离子Cr(VI)广泛应用于制革、电镀、印刷、颜料和抛光等行业, 因而成为地表水和地下水中常见的污染物。光催化还原Cr(VI)为Cr(III)利用可持续能源太阳能, 费用低且没有二次污染问题, 已经受到广泛关注。g-C₃N₄是一种稳定性好且能吸收可见光的优异光催化材料, 但也具有比表面积小及电子和空穴容易复合等缺点。为进一步提高g-C₃N₄的光

催化效率, 人们合成了各种新型复合材料, 如 $\text{g-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$, $\text{g-C}_3\text{N}_4/\text{SiW}_{11}$ 和 $\text{g-C}_3\text{N}_4/\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2(\text{H}_2\text{O})_2$ 等。

本文通过非常简便的球磨-煅烧法制备了金属-有机骨架材料MIL-100(Fe)与类石墨结构氮化碳($\text{g-C}_3\text{N}_4$)的异质结结构(MG- x , $x = 5\%$, 10% , 20% 和 30% , 代表MIL-100(Fe)占复合物的质量分数), 并对复合材料进行了粉末X射线衍射(PXRD)、红外光谱(FITIR)、热重(TGA)、透射电镜(TEM)、紫外-可见漫反射光谱(UV-Vis DR)和荧光光谱(PL)等表征。实验研究了MG- x 在模拟太阳光照射下光催化还原Cr(VI)和降解双氯芬酸钠的性能, 考察了空穴捕捉剂(乙醇、柠檬酸、草酸和双氯芬酸钠)和pH值(2–8)对光催化还原Cr(VI)效率的影响。

实验结果表明, PXRD谱图显示复合物的衍射峰位置均与MIL-100(Fe)及 $\text{g-C}_3\text{N}_4$ 的峰位置相吻合, 球磨和煅烧后无新衍射峰产生。TEM图片证明复合物中 $\text{g-C}_3\text{N}_4$ 附着在MIL-100(Fe)表面。光照80 min后, MG- x 复合物的还原效率均大于92%, 高于MIL-100(Fe)(75.6%)和 $\text{g-C}_3\text{N}_4$ (79.8%)的还原效率。其中, MG-20%的光催化活性最高, 还原效率达到97.0%, 且还原Cr(VI)的速率分别是MIL-100(Fe)的3.08倍和 $\text{g-C}_3\text{N}_4$ 的2.31倍。随着MIL-100(Fe)含量的增加, 复合物的光催化活性先增后减。这是因为MIL-100(Fe)含量的增加不仅有利于电荷的转移, 也有利于可见光的利用, 然而过多的MIL-100(Fe)可能会影响异质结的质量, 不利于电荷的转移。随着溶液pH值从2提高到8, 还原效率从98%降低到9%。这是因为在酸性条件下 H^+ 浓度高有利于Cr(VI)还原为Cr(III), 而当 $\text{pH} > 6$ 时, Cr^{3+} 与 OH^- 形成 $\text{Cr}(\text{OH})_3$ 沉淀附着在催化剂表面, 影响对光的吸收, 降低了光催化效率。当反应体系中加入乙醇、柠檬酸和草酸时, 光催化速率提高, 而加入双氯芬酸钠后光催化速率未见提高, 这是由于小分子链烃有机物容易捕捉光生空穴, 而双氯芬酸钠不能有效捕捉MG-20%产生的光生空穴。电化学测试证明 $\text{g-C}_3\text{N}_4$ 的光生电子可转移到MIL-100(Fe)的导带, 复合物提高了光生电子和光生空穴的分离效率, 从而提高了光催化还原Cr(VI)的活性。同时, 在加入 H_2O_2 的条件下, MG-20%在50 min内光催化降解双氯芬酸钠的效率达到100%。MG-20%循环使用5次后, 光催化效率没有明显降低, 光催化剂的XRD谱没有发生明显变化, 证明其具有很好的稳定性。综上, 本研究提供了一种具有应用前景的高效MOF/ $\text{g-C}_3\text{N}_4$ 复合物光催化剂。

关键词: MIL-100(Fe); $\text{g-C}_3\text{N}_4$; 异质结; 六价铬还原; 双氯芬酸钠

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