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Boosting the photoreduction activity of Cr(VI) in metal-organic frameworks by photosensitiser incorporation and framework ionization

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It is mandatory to decontaminate Cr(VI) species from water streams due to their high toxicity. The photoreduction of hazardous Cr(VI) to nontoxic Cr(III) is a very promising approach to harness Cr(VI) pollution. Althouth some MOFs and their composites have been employed as photocatalysts to reduce toxic Cr(VI), their catalytic activities always limited by inefficent visible light adsorption and inferior Cr(VI) adsorptive performances. Herein, a cationic Ru-UiO-dmbpy(1) that decorated with high density of cationic charges and as well embeded catalytically competent and visible light havesting moiteis (i.e. $Ru(bpv)_3$) was successfully synthesized by a sequential mix-and-match and ionization process. The presence of $Ru(bpv)_3$ moieties makes Ru-UiO-dmbpy(1) an excellent visible-light harvester, extending the adsortpion edge from 420 nm for pristine UiO-bpy to about 780 nm for Ru-UiO-bpy/Ru-UiO-dmbpy(1). Driven by ion exchange, Ru-UiO-dmbpy(1) shows a large adsorption rate constant (k_2) of 1.33×10⁻² g mg⁻¹ min⁻¹ in the adsorption of Cr₂O₇²⁻, which is 8.26 times that of pristine UiO-bpy and 6.27 times that of non-ionization counterpart Ru-UiO-bpy(1) under the same adsorption conditions. The equlibrium Cr₂O₇²⁻ uptake capacity of Ru-UiO-dmbpy(1) reaches to 101.8 mg/g, which is about 1.98 and 1.81 times that of UiO-bpy and Ru-UiO-bpy(1), respectively. With an efficient visible light absorption ability and superior Cr(VI) adsorption performance, Ru-UiO-dmbpy(1) shows a reaction rate constant (k_1) of 0.011 min⁻¹ in the photorduction of Cr(VI) without any sacrifice agents under visible light illumination, which is much larger than those of prinstine UiO-bpy (0.003 min⁻¹) and its non-ionization counterpart Ru-UiO-bpy(1) (0.007 min⁻¹) under the same conditions. The result umambiguously demonstrats the Cr(VI) photoreduction activity could be largely enhanced by photosensitiser introduction and framework ionization. To further evaluate the catalytic performance of Ru-UiO-dmbpy(1), Cr(VI) reduction was also investigated in the presence of various sacrifice agents. Remarkably, a high Cr(VI) photoreduction rate of 13.3 mg_{Cr(VI)}/g_{catalyst}/min was obtained when benzyl alcohol was used as sacrifice agent, which is a recorded value among the reported MOF-based photocatalysts.

1. Introduction

The massive use of hexavalent chromium Cr(VI) in modern industries including chromium electroplating, leather tanning, pigment production, metallurgy *etc.* has resulted in unneglectable Cr(VI) pollution worldwide.¹ Cr(VI) is carcinogenic, which is classified into a priority pollutant by the U.S. Environment Protection Agency (EPA).² Several technologies including ion exchange,³ adsorption,⁴ membrane separation,⁵ and photocatalytic reduction⁶ have been proposed to address Cr(VI) pollution. Among them, photocatalytic reduction that transforms toxic Cr(VI) species into

environmental benign Cr(III) is regarded as the most prospective technique due to its efficiency, low cost, no hazardous chemicals production, and energy conservation.⁷ An array of semiconductors including TiO₂, ZnO, CdS, C₃N₄ and their derivatives/composites have been employed as photocatalysts to reduce Cr(VI) in water media.⁸ However, their reduction activities under visible light irradiation are usually limited by poor Cr(VI) adsorptive ability, inferior visible light harvesting, fast recombination of photoinduced carriers and *etc.*⁹ Therefore, it is still a daunting challenge to develop new photocatalysts to tackle the above problems for efficient reduction of toxic Cr(VI).

Metal-organic frameworks (MOFs), comprising of organic ligands and metal ions, have gained immense attention in the last three decades. Due to their large specific surface area, designable structure, modulatable pore functionalization, MOFs have been widely applied in adsorption,^{10, 11} separation,¹² sensing,¹³⁻¹⁶ heterogeneous catalysis,^{17, 18} and so on. MOF-based photocatalysts could be regarded as a new type of semiconductor, whose HOMO-LUMO gaps could be considered as their band gaps.¹⁹ Benefiting from the adjustable chemical compositions, the band gap of MOFs can be finely tuned in the

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molecular level. In this regard, MOF-based photocatalysts could superior to traditional inorganic semiconductor be photocatalysts whose band gaps are difficult to adjust. In this context, several water-tolerant MOFs like ZIF-8, MIL-68(Fe), MIL-53(Fe), and MIL-100(Fe) have been employed as photocatalysts to reduce Cr(VI) in water medium under visible light illumination.²⁰⁻²⁴ These MOFs, however, cannot effectively absorb visible light, inhibiting their reduction performances. To extend the absorption edge to visible light region, organic linker decoration or photosensitizer incorporation were adopted to reduce the bandgap of MOFs and improve the visible light utilization. For example, by graft of amino groups into BDC²⁻ ligands, Wu et al. reported that MIL-68(In)-NH₂ has a better photoreduction activity than its unfunctional MIL-68(In) counterpart due to the extension of the absorption edge to visible region.²⁵ Ye and Cao et al. successfully introduced porphyrin units (a typical photosensitizer) into UiO-66 type framework, whose photoreduction activity is much higher than that of pristine UiO-66.²⁶ Compared with traditional inorganic semiconductors, another important merit of MOFs is their open framework, which could effectively inhibit the recombination of photogenerated electron-hole pairs due to their short spatial transmission distance. The photogenerated electrons or holes can facilely move to the substrates that interpenetrate into the cavies of the frameworks and quickly proceed redox reactions. Therefore, the mass transfer of substrates over MOF-based catalysts is an another vital parameter for Cr(VI) photoreduction. Albeit, most work only concerns the modulation of visible light absorption performance, and the effect of Cr(VI) adsorption over MOF catalysts is overlooked. Therefore, it is highly desirable to investigate the relationship Cr(VI) adsorption performances and between the photoreduction activities for the further development of efficient photocatalysts to reduce Cr(VI).

 $Ru(bpy)_{3^{2+}}$ (bpy = 2,2'-bipyridine) and its derivatives, an representative type of photosensitizers who can efficiently harvest photons within visible light, are one of the most attracting molecular photocatalysts.27 Various photocatalytic reactions have been successfully established in terms of their long lifetime of MLCT state and their easiness to undergo redox quenching.²⁸ Lin et al pioneered to incorporate Ru(bpy)₃²⁺ moieties into MOFs to study their application in photocatalysis.²⁹⁻³² Although many progresses have been made, the application of MOFs embedding Ru(bpy)₃²⁺ units for photoreduction of toxic Cr(VI) has not yet been reported. Herein, Ru-UiO-dmbpy(1) embedding Ru(bpy)₃²⁺ moieties and decorating with high density of cationic charges was synthesized by photosensitizer introduction and framework ionization. The physical properties, Cr(VI) adsorption performances, and Cr(VI) photoreduction behaviors of Ru-UiOdmbpy and the pristine sample UiO-bpy and its non-ionization counterpart Ru-UiO-bpy(1) were fully investigated. Besides, a mechanism concerning the Cr(VI) reduction was also proposed.

2. Experimental

2.1 Materials and methods

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2.1.1 Materials [2,2'-bipyridine]-5,5'-dicarboxylic of the distribution of the distributication of the

 $[Ru(bpy)_2(bpydc)]Cl_2$ (denoted as $Ru(bpy))^{29}$ and MOF-867³³ (denoted as UiO-bpy hereafter for convenience) were synthesized according to the reported literatures.

2.2 Synthesis of Ru-UiO-dmbpy

The synthetic process of Ru-UiO-bpy is similar to that of MOF-867 or UiO-bpy.²⁹ Taking Ru-UiO-bpy(1) as an example, DMF (7.2 mL) and glacial acetic acid (0.4 mL) were added to a Teflonlined stainless steel vessel (21 mL) containing a mixture of $ZrCl_4$ (46.7 mg, 0.2 mmol), 2,2'-bipyridine-5,5'-dicarboxylate (H₂bpydc) (48.8 mg, 0.2 mmol), and Ru(bpy) (4.6 mg, 0.02 mmol). The resulting mixture was sonicated for about 20 min. Subsequently, the vessel was placed in an oven and heated at 120 °C for 24 hours. After naturally cooling, an orange solid was isolated by centrifugation, sequentially washed with clean DMF and methanol, and then dried at 60 °C overnight under vacuum to get Ru-UiO-bpy(1) sample.

The N-methylation of open 2,2'-bpy units in Ru-UiO-bpy(1) was proceed as followings.³³ Excessive methyl trifluoromethanesulfonate (TfOMe, 1 mL) was added to a vial containing 50 mg of Ru-UiO-bpy(1) (0.023 mmol) to form a suspension. The suspension was stirred at room temperature for about 5 h. The solid was isolated by centrifugation, washed with ethanol, and then dried at 60 °C under vacuum overnight to get N-methylated sample Ru-UiO-dmbpy(1).

By tuning the feeding molar ratio of H_2 bpydc to Ru(bpy) from 10:2 and 10:0.5, two other materials denoted as Ru-UiO-bpy(2) and Ru-UiO-bpy(0.5) respectively were also synthesized by the same procedure. After N-methylation, the corresponding materials were denoted as Ru-UiO-dmbpy(2) and Ru-UiO-dmbpy(0.5), respectively.

2.3 Physical measurements

Powder X-ray diffraction (PXRD) was carried out on a Rigaku MiniFlex2 diffractometer working with Cu K α radiation. Fourier transform infrared (FT-IR) spectra were measured on a PerkinElmer Spectrum One. Inductively coupled plasma (ICP) measurements were performed on an Ultima2 spectrometer; To monitor Ru and Zr leaching by ICP, the reaction solution after photocatalytic reaction was filtered by a syringe filter (0.24 μ m) prior to ICP measurements. Solid UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was tested on a Shimadzu UV-2600 with BaSO₄ as the reference and transformed to the absorption spectra based on the Kubelka-Munk relationship. Fluorescent spectra were collected on a FS5 Spectrofluorometer (Edinburgh Instruments Ltd.). Fluorescent lifetimes were measured on a FLS980 Spectrofluorometer (Edinburgh Instruments Ltd.) with the excitation wavelength of 475 nm and monitoring wavelength of 650 nm. Scanning electron microscopy (SEM) images were collected in JSM6700-F and SU-8010 field emission microscopes. scanning electron X-ray photoelectron

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spectroscopy (XPS) was measured on an ESCALAB 250Xi Xray photoelectron spectrometer (Thermo Fisher) using an Al K α source (15 kV, 10 mA). ¹H NMR was performed on an AVANCE III Bruker Biospin spectrometer (400 MHz). N₂ sorption isotherms were performed at 77 K on a Micrometrics ASAP 2460 surface area and pore size analyser. Electron paramagnetic resonance (EPR) spectra were collected on a Bruker-BioSpin E500 spectrometer at room temperature. Perfectlight (PLS-SXE300) with a 300 W xenon lamp equipped with an ultraviolet cut-off filter (> 420 nm) was used as the irradiation source.

2.4 Electrochemistry measurements

The catalyst-modified electrode was prepared on a fluorine doped tin oxide (FTO) glass. The FTO slide was previously protected using Scotch tape to make sure that the exposed area of the working electrode was controlled at 1.0 cm². 5 mg of photocatalyst, 0.7 mL of DMF, and 0.3 mL of alcohol was mixed and sonicated to get a homogeneous slurry. FTO slide was dip coated with 60 μ L of the above-prepared slurry. After air drying, the working electrode was further dried at 70 °C for 24 h to improve adhesion. All the electrochemical station (Zahner, Germany) in a three-electrode quartz cell. The Mott-Schottky and photocurrent analyses were measured in 0.2 M Na₂SO₄ aqueous solutions, which were purged with N₂ before measurements. The light irradiation source was the same as that used in the photocatalytic tests.

2.5 $Cr_2O_7^{2-}$ adsorption experiments

Prior to the adsorption experiments, $Cr_2O_7{}^{2-}$ aqueous solutions with preset concentrations were prepared. The pH of $Cr_2O_7{}^{2-}$ aqueous solutions was adjusted by 0.1 M of HCl and NaOH.

2.6 Photocatalytic tests

Typically, the photocatalytic experiment was carried out as following steps. 10.0 mg of photocatalyst and 40 mL of $Cr_2O_7^{2-}$ aqueous solution with an initial concentration of 50 ppm were placed in a 200-mL quartz reactor. The mixture was vigorously stirred in the dark for 1 hour to reach $Cr_2O_7^{2-}$ adsorption-desorption equilibrium over the catalyst. Subsequentially, the reactor was illuminated by visible light. During this process, 1.0 mL of the suspension was taken from the reactor at pre-set time interval, filtered by a syringe filter, and the $Cr_2O_7^{2-}$ concentration in the filtrate was measured by UV–vis spectroscopy using the DPC method. The reduction percentage of Cr(VI) was calculated by the following equation:

Reduction percentage of Cr(VI) (%) = $(C_0 - C_t)/C_0 \times 100\%$ where C_0 and C_t are the Cr₂O₇²⁻ concentration when the reaction system was illuminated at 0 and *t* min, respectively.

The cycled experiment was carried out as followings. After reaction, Ru-UiO-dmbpy(1) was collected by centrifugation, washed sequential by NaCl aqueous solution, 0.1 M HNO₃ solution, and ethanol. The solid then dried under vacuum at 60 °C overnight for the next run.



Fig. 1 Synthetic procedure of (a) UiO-bpy, as well as (b) Ru-UiO-bpy and Ru-UiO-dmbpy.

During the Cr(VI) photoreduction process, the Cr(VI) adsorption and desorption over the catalysts occur simultaneously. It is difficult to calculate the exact amount of

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Cr(VI) reduced. For convenience, we assume that the adsorbed Cr(VI) proportionately decreases with that in the reaction solutions. It is reasonable because all Cr(VI) were completely reduced under the optimal conditions.

3. Results and discussion

3.1 Structure and Characterization

UiO-bpy (i.e., MOF-867, Fig. 1a), a thermal-stable and watertolerant MOF that is self-assembled by ZrCl₄ and 5,5'-dicarboxy-2,2'-bipyridine (H₂bpydc) ligand, was selected as the platform to introduce the photosensitiser and catalytically competent Ru(bpy). As shown in Fig. 1b, Ru-UiO-bpy was synthesized by the mix-and-match strategy, whose synthetic procedure is similar to that of UiO-bpy except that H₂bpydc is partially replaced with Ru(bpy). PXRD result confirms that Ru-UiO-bpy retains UiO-bpy type framework when the feeding molar ratio of Ru(bpy) to H₂bpydc is smaller than 2:10 (Fig. 2a and S1). The successful Nmethylation of 2,2'-bpy moieties in Ru-UiO-bpy is verified by the appearance of three new adsorption peaks at about 1263, 1174 and 1032 cm⁻¹ in the IR spectra of Ru-UiO-dmbpy samples (Fig. 2b and S4), which could be assigned to TfO⁻ anions that serve as counterions in the cavities of cationic Ru-UiO-dmbpy framework.³³ Taking Ru-UiO-dmbpy(1) as an example, about 89% of 2,2'-bpy moieties have been N-methylated, as indicated by the ¹H NMR spectrum of the digested Ru-UiO-dmbpy(1) sample where about 71% of dimethylated product and about 18% of monomethylated ligands are observed (Fig. S9-10).

PXRD patterns of Ru-UiO-dmbpy(1) and Ru-UiO-bpy(1) match well with those of experimental and stimulated UiO-bpy, demonstrating the good retention of UiO-bpy/MOF-867 type structure after photosensitiser introduction and N-methylation (Fig. 2a and S2). The Brunauer-Emmett-Teller (BET) surface areas and pore volumes are 1367 $m^2 \: g^{\text{-1}}$ and 0.956 $\text{cm}^3 \: g^{\text{-1}}$ for UiO-bpy, and 692 m² g⁻¹ and 0.829 cm³ g⁻¹ for Ru-UiO-bpy(1), which further decreased to 174 m² g⁻¹ and 0.205 cm³ g⁻¹ for Ru-UiO-dmbpy(1) (Fig. 2c and Fig. S5). Such a large decrement in both the surface area and pore volume of Ru-UiO-dmbpy(1) is attributed to cavity occupancy by the introduced Ru(bpy)₃ moieties, pyridyl N⁺–CH₃ groups, and also the TfO⁻ counterions. Scanning electron microscopy (SEM) images reveal that Ru-UiOdmbpy(1) shows distorted octahedral particles with sizes of ranging from 50 to 100 nm (Fig. 2d). ¹HNMR spectrum of HFdigested Ru-UiO-dmbpy(1) sample reveals that the molar ratio of H₂bpydc to Ru(bpy) is about 18.2 (Fig. S9), indicating that about one in nineteen of H₂bpydc is replaced with Ru(bpy) ligand. ICP measurement show that the molar ratio of Zr to Ru in Ru-UiO-dmbpy(1) is 17.9 (Table S1), corresponding to one in eighteen H₂bpydc is replaced with Ru(bpy), matching well with the ¹H NMR result. The incorporation of Ru(bpy)₃ moieties into UiO-bpy type structure results in tremendous change of UV-vis diffuse reflectance spectra. As shown in Fig. 3a, the absorption wavelength edge is extended from 420 nm for UiO-bpy to ca.



Fig. 2 (a) PXRD patterns of UiO-bpy, Ru-UiO-bpy(1) and Ru-UiO-dmbpy(1). (b) FT-IR spectra and (c) N_2 adsorption isotherms of UiO-bpy, Ru-UiO-bpy(1) and Ru-UiO-dmbpy(1). (d) SEM image of the as-synthesized Ru-UiO-dmbpy(1) sample.

780 nm for Ru-UiO-bpy(1)/Ru-UiO-dmbpy(1), corresponding to the colour change from white for UiO-bpy to dark orange for Ru-UiO-bpy(1)/Ru-UiO-dmbpy(1) (Fig. 3b). The broad absorption band in the visible light for Ru-UiO-bpy(1)/Ru-UiO-dmbpy(1) is mainly attributed to the metal-to-ligand charge transfer (MLCT) of the incorporating Ru(bpy)₃ moieties.³⁴



Fig. 3 (a) UV-visible diffuse reflectance spectra of H_2 bpydc, Ru(bpy), UiO-bpy, Ru-UiO-bpy(1) and Ru-UiO-dmbpy(1), respectively. (b) Photographs of their powdery samples.

3.2 Cr(VI) adsorption behaviours on photocatalysts

The incorporation of Ru(bpy)₃ photosensitiser and the high porosity of Ru-UiO-bpy/Ru-UiO-dmbpy inspired us investigate their photoreduction of toxic Cr(VI) under visible light irradiation. MOFs can be seen as nano-scale inorganic semiconductor/photosensitiser composites When the metal clusters and organic ligands are separately considered as nanoscale semiconductor guantum dots and photosensitisers respectively. One of the prerequisites to initiate the photocatalytic redox reaction is close contact between the nanocatalysts and substrates that facilitates the electron/hole transfer. Therefore, the adsorption efficiency of Cr₂O₇²⁻ over photocatalysts is closely related to the Cr(VI) photoreduction activity. Keeping this in mind, Cr₂O₇²⁻ adsorptive performance over these MOF-based catalysts was evaluated in aqueous solutions at pH 3. As shown in Fig. S11, with only 0.25 g L⁻¹ adsorbent dosage and within 30 min, Ru-UiO-dmbpy(1) could

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adsorb about 49.4% of $Cr_2O_7^{2-}$ in an aqueous solution with an initial $Cr_2O_7^{2-}$ concentration of 50 ppm (40 mL), confirming the high adsorption efficiency of $Cr_2O_7^{2-}$ over Ru-UiO-dmbpy(1). Under this condition, the maximum Cr₂O₇²⁻ uptake over Ru-UiOdmbpy(1) reaches to 101.8 mg/g, which is 1.81 times that of its non-ionized counterpart Ru-UiO-bpy(1) (56.3 mg/g) and about 1.98 times that of pristine UiO-bpy (51.4 mg/g) (Fig. 4b). Considering that the order of BET surface areas and pore volumes is UiO-bpy > Ru-UiO-bpy > Ru-UiO-dmbpy, the reverse order of $Cr_2O_7^{2-}$ adsorption capacity under the same adsorption condition is mainly ascribed to the framework ionization. Ru-UiO-dmbpy(1), which has more negative counterions (i.e. F₃CSO₃⁻ and Cl⁻ counterions) in the cavities of framework than non-ionic counterpart Ru-UiO-bpy(1) (i.e. Cl⁻) and neutral UiObpy (no counterions) for ion exchange, shows largest $Cr_2O_7^{2-}$ uptake capacity. To investigate the Cr(VI) adsorption kinetics, the $Cr_2O_7^{2-}$ adsorption amount versus contact time are shown in Fig. 4b and these data are fitted by pseudo-second-order model (Fig S12). High correlation coefficients (> 0.989) are obtained, indicating that the Cr₂O₇²⁻ adsorption over UiO-bpy, Ru-UiO-bpy(1), and Ru-UiO-dmbpy(1) follow the pseudosecond-order model (Figure S12 and Table S2). Remarkably, Ru-UiO-dmbpy(1) also shows a highest adsorption rate than UiObpy and Ru-UiO-bpy(1), as demonstrated by the adsorption rate constant (k_2) at the same adsorption time under the same adsorption conditions. The adsorption rate constant (k_2) of Ru-UiO-dmbpy(1) reaches to 1.33×10^{-2} g mg⁻¹ min⁻¹ which is 8.26 times that of pristine UiO-bpy (2.87×10⁻³ g mg⁻¹ min⁻¹) and 6.27 times that of non-ionization counterpart Ru-UiO-bpy(1) (2.12×10⁻³ g mg⁻¹ min⁻¹). The initial adsorption rate h of Ru-UiOdmbpy(1) is 17.7 and 19.9 times that of UiO-bpy and Ru-UiObpy, respectively. The largest Cr(VI) adsorption capacity coupled with the highest Cr(VI) adsorption rate of Ru-UiO-dmbpy(1) demonstrated the importance of ionization process for the improvement of the Cr(VI) adsorption performance, which largely enhanced the mass transfer of Cr(VI) and could boost the photocatalytic activity of Cr(VI) reduction.



Fig. 4 (a) The pseudo-second-order adsorption rate constant (k_2) over UiO-bpy, Ru-UiO-bpy(1), and Ru-UiO-dmbpy(1), respectively. (b) Effect of the contact time on the adsorption amount of $Cr_2O_7^{2-}$ over UiO-bpy, Ru-UiO-bpy(1), and Ru-UiOdmbpy(1), respectively. Adsorption conditions: adsorbent, 10 mg; $Cr_2O_7^{2-}$ solution, 40 mL, 50 ppm; temperature, 25 °C; and pH, 3.0.

3.3 Photocatalytic reduction of Cr(VI)

To evaluate the photoreduction performance, the photocatalytic reaction was initially performed under the following conditions: 10 mg of photocatalyst, 40 mL of $Cr_2O_7^{2-}$

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aqueous solution with an initial concentration of 50, ppm, and pH of 3.0. Prior to visible light illumination; 1the 3mixture 3 was vigorously stirred in the dark for 1 h to reach adsorptiondesorption equilibrium of Cr(VI). As shown in Fig. 5a, no observable decrease of $Cr_2O_7^{2-}$ content is observed in the absence of catalyst after illumination by visible light for 120 min. Only about 29% of apparent Cr(VI) decrease (including adsorption and photoreduction) is found for UiO-bpy, 30% for mechanical mixture of Ru(bpy) and H₂bpydc, and 54% for Ru-UiO-bpy. Impressively, Ru-UiO-dmbpy(1) shows an excellent photocatalytic activity for Cr(VI) reduction and it could remove about 80% of Cr(VI) under the identical conditions. Control experiment shows that Cr₂O₇²⁻ concentration almost remained unchanged after further preservation in the dark for 2 h. Therefore, the Cr(VI) concentration decrease after adsorptiondesorption equilibrium is mainly ascribed to the visible light driven photodegradation. То further evaluate the photocatalytic behaviours of these MOFs, the experimental kinetic data were further fitted by the pseudo-first-order model and the results were shown in Figure 5b and Table S3. The Cr(VI) reduction over the mechanical mixture of Ru(bpy) and H₂bpydc, UiO-bpy, Ru-UiO-bpy(1), and Ru-UiO-dmbpy(1) obey the pseudo-first-order model, as demonstrated by the high correlation coefficients (> 0.946). The calculated rate constant of Ru-UiO-dmbpy(1) is 0.011 min⁻¹, which is about 1.6, 3.7, 5.5 times for mechanical mixture of Ru(bpy) and H₂bpydc (0.002 min⁻¹), UiO-bpy (0.003 min⁻¹), and Ru-UiO-bpy(1) (0.007 min⁻¹), respectively. In view of the very similar Cr(VI) adsorption performance between UiO-bpy and Ru-UiO-bpy(1), the larger photoreduction rate constant of Ru-UiO-bpy(1) could be ascribed to its more efficient visible light response. While the better Cr(VI) adsorption performance contributes to the larger rate constant of Ru-UiO-dmbpy(1) than that of Ru-UiO-bpy(1). The largest rate constant of Ru-UiO-dmbpy(1) indicates its highest activity in the Cr(VI) photoreduction, which can be well explained by the synergistic of efficient visible light harvesting and the excellent Cr(VI) adsorption performance. Besides, the presence of largest electrostatic attractions between anionic $Cr_2O_7^{2-}$ and cationic Ru-UiO-dmbpy(1) as well as the largest electrostatic repulsions between Cr3+ and cationic Ru-UiOdmbpy(1) may also improve the mass transfer of Cr³⁺ and Cr₂O₇²⁻, which also benefits for the Cr(VI) photocatalytic reduction activity. These results unambiguously demonstrate combination of photosensitizer introduction and the framework ionization is a very effect strategy to boost the Cr(VI) photoreduction activity.

Based on the above results, Ru-UiO-dmbpy(1) was chosen as representative photocatalyst to investigate its Cr(VI) photoreduction behaviours. For a typical photocatalytic process, the electron-hole pairs will be generated upon light irradiation. The separation efficiency of the photogenerated electrons and holes could be enhanced when the holes (h^+) are rapidly consumed, leading to the acceleration of the total redox reaction including Cr(VI) photoreduction half reaction. For this reason, some electron donors including methanol, ethanol, and ammonium oxalate have been employed as hole scavengers in the photoreduction of Cr(VI) to improve the photocatalytic

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activities.²⁵ Herein, triethanolamine (TEOA), methanol, ammonium oxalate (AO), and also benzyl alcohol (BA) were selected as sacrificial agents to promote the total redox reaction. As shown in Fig. 5c, benzyl alcohol significantly boosts the Cr(VI) photoreduction in comparison with other sacrificial agents (including no additional sacrificial or water as sacrificial agent). Therefore, benzyl alcohol was selected as the sacrificial agent in this Cr(VI) photoreduction system.

pH value is another vital parameter to affect the photoreduction activity of Cr(VI). Previous studies reveals that Cr(VI) photoreduction activity could be enhanced at low pH.³⁵ As expected, the photocatalytic activity of Ru-UiO-dmbpy(1) also strongly relied on pH (Fig. 5d). At pH 3.0, Ru-UiO-dmbpy(1) could completely reduce Cr(VI) under visible light irradiation for 30 min. Under the same conditions, however, the apparent Cr(VI) reduction percentage significantly decreases to 65.7% for pH 4 and 70% for pH 5, respectively. The catalytic efficiency lowing is further confirmed by the rate constant decreasing with the pH increasing, which is obtained from kinetic data fitted by the pseudo-first-order kinetic model (Fig. S14). The decline of photocatalytic activity under low acidic environments is not only ascribed to the decrement in oxidation potential of $Cr_2O_7^{2-}$, but also ascribed to the potential formed Cr(OH)₃ precipitates that could block the cavities of the framework and mask the photoactive sites.³⁶ Therefore, the optimal pH was 3.0, and the following experiments were conducted at this pH value.

To evaluate the effect of the incorporated Ru(bpy)₃ content to photoreduction activity, the as-synthesized three Ru-UiOdmbpy frameworks are screened under the optimal photocatalytic conditions. Fig. 5e showed that the Cr(VI) photoreduction activity first enhances and then declines with the increment in the feeding ratio of H₂bpydc to Ru(bpy) from 10:0.5 to 10:2 and the optimal ligand feeding ratio is found at 10:1 (corresponding to Ru-UiO-dmbpy(1) material). Ru-UiOdmbpy(1) has a rate constant of 0.128 min⁻¹, which is much larger than those of Ru-UiO-dmbpy(0.5) (0.025 min⁻¹) and Ru-UiO-dmbpy(2) (0.043 min⁻¹), matching well with the above order of photocatalytic efficiency (Fig. 5f, S15 and Table S4). The preliminary increase of Ru(bpy) ligand would increase the photocatalytic active sites and enhance the visible light harvesting. However, further increase of the Ru(bpy) amount will deteriorate the framework crystallinity due to the large steric hindrance of Ru(bpy)₃ moieties (Fig. S1-2). In addition, Ru(bpy)₃ moieties also inevitably blocked the cavities of Ru-UiOdmbpy, lowing the accessibility of photocatalytic sites and deteriorating the mass transfer of the subtract. The rate constant of Ru-UiO-dmbpy(1) is larger than those of the recently reported representative inorganic-based photocatalysts including OH-TiO₂ (0.079 min⁻¹),³⁷ g-C₃N₄/BiVO₄ (0.063 min^1), 38 and g-C_3N_4/SnS_2/SnO_2 (0.0517) 39 but a little smaller than BMO-S1 (0.164 min⁻¹)⁴⁰ and CdS-ZnIn₂S₄ (0.179 min⁻¹).⁴¹ Specially, such a larger rate constant is comparable to that of H₂TCPP_{(I})Meim-UiO-66 (0.1541 min⁻¹)²⁶ and only much smaller than that of Pt@MIL-100(Fe) (0.5618 min⁻¹)⁴² among the MOF-based photocatalysts, verifying the high catalytic activity of Ru-UiO-dmbpy(1) in Cr(VI) photoreduction under visible light irradiation.

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To further confirm the effectiveness of Ru-UiO₂dmbpy(1) in the photoreduction of Cr(VI), the photoeatalytie approximation were also carried out in aqueous solutions with various initial contents of $Cr_2O_7^{2-}$. As shown in Fig. S16, Ru-UiO-dmbpy(1) could completely reduce Cr(VI) in aqueous solutions of Cr₂O₇²⁻ (40 mL) with an initial $Cr_2O_7^{2-}$ concentration lower than 100 ppm within 30 min. Notably, the photoreduction rate reaches to 13.3 $mg_{Cr(VI)}/g_{catalyst}/min$ when the initial concentration of $Cr_2O_7^{2-}$ was 100 ppm. This value is equal to that of H₂TCPP⊂(I⁻)Meim-UiO-66,²⁶ and much larger than those of the representative MOFbased catalysts like NH₂-UiO-66 (0.2 mg_{Cr(VI)}/g_{catalyst}/min),²³ NH₂-MIL-125 (1.6 mg_{Cr(VI)}/g_{catalyst}/min),⁴³ Pt@MIL-100(Fe)/40 (1.3 mg_{Cr(VI)}/g_{catalyst}/min),⁴² and HPMo@MIL-100(Fe)/20 (5.0 $mg_{Cr(VI)}/g_{catalyst}/min$).²² As far as we know, this value represents the largest reduction rate among MOF-based photocatalysts for Cr(VI) reduction (Table S9). Such a high reduction rate is mainly ascribed to the excellent Cr₂O₇²⁻ adsorption performance and excellent visible light utilization. The above result confirms that it is an effective strategy to construct efficient photocatalysts for Cr(VI) photo-degradation under visible light illumination via photosensitiser introduction and framework ionization.



Fig. 5 (a) Photocatalytic experiments under the initial reaction conditions and (b) Plots of $\ln(C/C_0)$ versus time for Cr(VI) reduction over various catalysts. The effects of (c) hole scavengers, (d) pH values, (e) Ru-UiO-dmbpy composites on the Cr(VI) photoreduction performance and (f) K value over various Ru-UiO-dmbpy composites.

XPS was employed to determine the photoreduction product. As shown in Fig. S18, a couple of peaks with binding energies of 577.2 eV and 587.2 eV is observed in Ru-UiO-dmbpy(1) after photocatalytic reaction, which can be assigned to Cr 2p^{3/2} and Cr 2p^{1/2} of Cr³⁺, respectively. The absence of binding energies of Cr(VI) at 580 eV for and 589 eV for hexavalent chromium species

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further indicates all the toxic Cr(VI) species have been reduced to $\rm Cr^{3+}$ during photoreduction process.^{44}

3.4 Recycling experiments

The recoverability and reusability of a heterogeneous catalyst is pivotal for their practical applications.⁴⁵ Ru-UiO-dmbpy(1) could be recovered by centrifugation and washing with an aqueous solution of HNO_3 (0.1 M). The photocatalytic activity of the recovered Ru-UiO-dmbpy(1) almost remains unchanged after seven successive runs (Fig. 6). Benefiting from the high stability of UiO-type framework, the recycled Ru-UiO-dmbpy(1) could well retain its structure, as demonstrated by PXRD (Fig. S19). The morphologies of the pristine and recycled samples are very similar to each other (Fig. 2d, S20), and only a very low Ru leaching of less than 0.185 ppm was detected even in the seventh photocatalytic run (Table S6). Besides, the BET surface area of the recycled Ru-UiO-dmbpy(1) is 293.1 m² g⁻¹, which is larger than that of as-synthesized Ru-UiO-dmbpy(1) sample (i.e., 174 m² g⁻¹) (Fig. S21). The larger BET surface area of Ru-UiO-dmbpy(1) can be well explained by the partial replacement of larger CF₃SO₃⁻ by smaller Cl⁻, as verified by the EDS spectrum where the molar ratio of Cl⁻ increases from 14.5 (calculated value) for the as-synthesized Ru-UiO-dmbpy(1) to 1.28 (experimental value) for the recycled sample (Fig. S22). These results further confirm the good stability of Ru-UiO-dmbpy(1) photocatalyst. The good reusability and high chemical/photostability of Ru-UiO-dmbpy(1) makes it a very promising photocatalyst for Cr(VI) decontamination in practical applications.



Fig. 6 Reusability of Ru-UiO-dmbpy(1) for the photoreduction of $Cr_2O_7^{2-}$ under irradiation by visible light for 30 and 60 min.

3.5 Plausible Mechanism

The above experimental results have shown that Ru-UiOdmbpy(1) is an better material than pristine UiO-bpy and its non-ionization counterpart Ru-UiO-bpy(1) for the adsorption and photoreduction of $Cr_2O_7^{2^-}$. To fully understand the photocatalytic mechanism, the band structure of the catalysts, the separation efficiency and transfer processes of the photogenerated charge carries over the these photocatalysts are discussed detailly.

Mott-Schottky plots and UV–vis DRS were used to investigate the band structure of the catalysts. Based on the result of Mott-Schottky plots at different frequencies (i.e., 500, 1000, and 1500 Hz) (Fig. 7a-c, S23), the lowest unoccupied molecular orbitals

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(LUMO) of UiO-bpy, Ru-UiO-bpy(1), and Ru-UiO-dmbpy(1), were -0.84, -0.88, and -0.92 V vs Ag/AgCl at phpl=16.1837espectavely, corresponding to -0.64, -0.68, and -0.72 V vs normal hydrogen electrode (NHE). The flat-band potentials of these materials are more negative than the electrode potential of $Cr_2O_7^{2-}/Cr^{3+}$ (i.e., 0.51 V vs NHE at pH = 6.8), verifying their feasibilities as photocatalysts to reduce Cr₂O₇²⁻ since the electrons theoretically could transfer from these materials to Cr₂O₇^{2-.46} The slopes of the Mott-Schottky plots are all positive, indicating that these materials could be regarded as *n*-type semiconductor where the conductive band potential can be regarded as the flat-band potential. According to the Tauc plots (Fig. 7d-f, Fig. S23), the bandgap of UiO-bpy was 3.53 eV, which decreased to 2.16 V for Ru-UiO-bpy(1) and 2.13 V for Ru-UiO-dmbpy(1) respectively, corresponding to the absorption wavelength edge ranging from 420 nm for UiO-bpy to about 780 nm for Ru-UiObpy(1)/Ru-UiO-dmbpy(1). The highest occupied molecular orbital (HOMO) of UiO-bpy, Ru-UiO-bpy, and Ru-UiO-dmbpy(1) are 2.89, 1.48, and 1.41 V vs normal hydrogen electrode (NHE), respectively, which are obtained from the band gap and LUMO (Fig. 7a-c). Compared with UiO-bpy, Ru-UiO-dmbpy(1)/Ru-UiObpy(1) have a more suitable band structure and wider visible light absorption, making them as better photocatalysts than UiO-bpy to reduce $Cr_2O_7^{2-}$ under the visible light illumination.



Fig. 7 Typical Mott–Schottky plots for (a) UiO-bpy, (b) Ru-UiO-bpy(1) and (c) Ru-UiOdmbpy(1) at frequencies of 500, 1000 and 1500 Hz. Tauc plots and bandgaps for (d) UiObpy (e) Ru-UiO-bpy(1) and (f) Ru-UiO-dmbpy(1).

In principle, a low resistance and a small arc radius in an EIS Nyquist plot means a fast charge transfer in a semiconductor, which could enhance the separation efficiency of electron and hole pairs and thus improves the photocatalytic activity. As shown in Fig. 8a, Ru-UiO-dmbpy(1) has a smaller radius and a lower transfer resistance than UiO-bpy and Ru-UiO-bpy(1), implying the faster interfacial charge transfer in Ru-UiOdmbpy(1). The result matches well with the experimental results where Ru-UiO-dmbpy(1) shows a higher catalytic activity for Cr(VI) reduction than UiO-bpy and Ru-UiO-bpy(1). (Fig. 5a). The transient photocurrent spectra of UiO-bpy, Ru-UiO-bpy(1), and Ru-UiO-dmbpy(1) were collected under the intermittent visible light illumination (> 420 nm). An apparent photocurrent response of MOFs coated electrodes in an off-on mode was detected (Fig. 8b), confirming the competence of these MOFs in the production and transfer of photogenerated electrons and holes under visible light illumination. Among them, Ru-UiOdmbpy(1) shows a largest photocurrent upon visible light illumination, implying the best photocatalytic activity of Ru-UiO-dmbpy(1).

The separation of the photogenerated electron and hole pairs could be further analyse by steady-state photoluminescent spectrum. To some extent, the luminescent intensity reflects the separation efficiency of electron-hole pairs, and a stronger luminescence usually implies better recombination and low separation efficiency. As shown in Fig. 8c, the photoluminescent intensities of Ru-UiO-dmbpy(1) is much weaker than that of Ru-UiO-bpy(1), indicating the obstruction of electron-hole recombination after framework ionization. Time-resolved luminescence was further employed to investigate the charge transfer process. Fig. 8d and Table S7 show the photoluminescent lifetime of Ru-UiO-dmbpy(1)



Fig. 8 (a) EIS Nyquist plots of UiO-bpy Ru-UiO-bpy(1) and Ru-UiO-dmbpy(1), respectively. (b) Transient photocurrent response of UiO-bpy Ru-UiO-bpy(1) and Ru-UiO-dmbpy(1) under the visible light irradiation (420 nm–780 nm). (c) Luminescent spectra of UiO-bpy Ru-UiO-bpy(1) and Ru-UiO-dmbpy(1) in DMF solution. (d) Time-resolved luminescent decay of Ru-UiO-bpy(1), Ru-UiO-dmbpy(1) suspensions before and after the in-situ addition of $Cr_2O_7^{2c}$.

suspension is 620 ns, which significantly shortens to 188 ns after in-situ addition of $Cr_2O_7^{2^-}$. Such an apparent lifetime shortening demonstrates that the long-lived photogenerated electrons are easily transferred from Ru(bpy)₃ moieties to $Cr_2O_7^{2^-}$.

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Electron paramagnetic resonance (EPR) analyses were used to study the electron transfer processes. As shown for the tiges of the processes of the tiges of the processes of the

Based on the above experimental results and related mechanisms previously reported, 10, 47, 48 a mechanism concerning the adsorption and photoreduction of $Cr_2O_7^{2-}$ over Ru-UiO-dmbpy(1) is proposed and illustrated in Fig. 9. Prior to reaction, the anionic $Cr_2O_7^{2-}$ are quickly adsorbed into the cavities of cationic Ru-UiO-dmbpy(1) via ion exchange. Upon irradiation by visible light, Ru(bpy)₃ moieties in Ru-UiOdmbpy(1) strongly absorb visible light and spontaneously generate photogenerated electron and hole pairs via metal-toligand charge transfer (MLCT).⁴⁹ Therefore, the photogenerated electrons mainly located at bpy, while the holes locate at Ru. Meanwhile, the photogenerated electrons on bpy could also transfer to Zr₆O₄(OH)₄ SBUs via ligand-to-metal charge transfer (LMCT) or dmbpydc²⁻ linkers via ligand-to-ligand charge transfer (LLCT). The combination of MLCT, LMCT and LLCT effectively separate the photogenerated electron-hole pairs, thus largely boosting the photocatalytic activities of Ru-UiO-dmbpy(1). The photogenerated electrons then involves in the reduction of Cr(VI), while the photogenerated holes are scavenged by benzyl alcohol. During the photocatalytic process, anionic Cr₂O₇²⁻ is preferred to be adsorbed into the cavities of cationic frameworks while the reductive product Cr³⁺ is prone to being precluded out due to the electrostatic interactions, which effectively improve the Cr(VI) adsorption performance of Ru-UiO-dmbpy(1). The excellent Cr(VI) adsorption performance of Ru-UiO-dmbpy(1) also effectively boosts the photocatalytic activities of Ru-UiO-dmbpy(1).



Fig. 9 The proposed mechanism of Cr(VI) photoreduction when Ru-UiO-dmbpy(1) acted as the photocatalyst under visible light irradiation.

Conclusions

In summary, Ru(bpy)₃ functionalized and ionized MOFs, Ru-UiOdmbpy, was successfully prepared *via* the mix-and-match synthetic strategy and ionization process. The introduction of photosensitive Ru(bpy)₃ moieties largely expanded the spectral

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response from 420 nm for UiO-bpy to about 780 nm for Ru-UiObpy(1)/Ru-UiO-dmbpy(1). The framework ionization endows Ru-UiO-dmbpy(1) with highest $Cr_2O_7^{2-}$ adsorption rate and largest $Cr_2O_7^{2-}$ uptake capacity *via* ion-exchange in comparation to pristine UiO-bpy and its non-ionized Ru-UiO-bpy(1) counterparts. As a result of the best $Cr_2O_7^{2-}$ adsorptive performance and efficient visible-light utilization, Ru-UiOdmbpy(1) shows a more efficiency in Cr(VI) photoreduction than UiO-bpy and Ru-UiO-bpy under visible light illumination. Further investigations show that Ru-UiO-dmbpy(1) can effectively reduce Cr(VI) to Cr(III) with a recorded reductive rate of 13.3 $mg_{Cr(VI)}/g_{catalyst}/min$ when benzyl alcohol acts as sacrificial agent. This work reveals the importance of substrate adsorption over the catalyst to photocatalytic efficiency and presents an effective strategy to boost Cr(VI) photoreduction activity by photosensitiser introduction and framework ionization.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Ru-UiO-dmbpy was successfully synthesized by sequential PS introduction and framework ionization, whose Cr(VI) photoreduction efficiency is largely boosted in comparation with the pristine UiO-bpy and non-ionized Ru-UiO-bpy counterpart due to the great improvement of the visible light harvesting ability and Cr(VI) adsorption performance.