

Construction of a $\text{CeO}_2/\text{ZnO}/\text{NH}_2\text{-MIL-101(Fe)}$ Ternary Heterojunction for Efficient Visible-Light-Driven Photocatalytic Reduction of U(VI) : Enhanced Charge Separation and Uranium Immobilization Mechanism

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Construction of a CeO₂/ZnO/NH₂-MIL-101(Fe) Ternary Heterojunction for Efficient Visible-Light-Driven Photocatalytic Reduction of U(VI): Enhanced Charge Separation and Uranium Immobilization Mechanism

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Abstract

The remediation of radioactive effluent is significantly impacted by the development of highly efficient visible-light photocatalysts for the reduction of soluble radionuclide. This study successfully synthesized and evaluated NH₂-MIL-101(Fe) (MIL) and a series of CeO₂/ZnO-modified NH₂-MIL-101(Fe) ternary heterojunctions (A-C) for the photocatalytic reduction of aqueous U(VI). After 60 min of visible-light irradiation, the optimized 5%CeO₂/10%ZnO/MIL (composite B) exhibited the highest photocatalytic activity among the prepared photocatalysts, achieving 92.9% and 95.1% under air and N₂ atmospheres, respectively. These experiments were carried out under the optimal conditions of 75 mg catalyst dosage, 20 mg L⁻¹ initial U(VI), pH 5, and 1% (v/v) formic acid. In addition, the effects of oxides loading, catalyst dosage, initial U(VI) concentration, solution pH, reaction atmosphere, sacrificial reagents, and catalyst recyclability were systematically investigated. Moreover, the successful construction of the CeO₂/ZnO/MIL heterojunctions was confirmed by comprehensive characterization using PXRD, FT-IR, XPS, UV-vis diffuse reflectance spectroscopy, N₂ adsorption-desorption, photoluminescence spectroscopy, and electrochemical impedance spectroscopy. Although the conventional binary heterojunctions possess a single semiconductor interface, the CeO₂/ZnO/MIL ternary architecture is composed of multiple coupled interfaces and the synergistic functions of the three components, which create more efficient interfacial pathways for directional charge migration. This cooperative interfacial effect promotes the electron transit and spatial charge separation, and suppresses the electron-hole recombination, hence enhancing the availability of reduction-active electrons toward U(VI). The characterization also revealed substantially enhanced visible-light harvesting, efficient interfacial charge separation, accelerated electron transport, and suppressed electron-hole recombination. Furthermore, the dominant reactive species responsible for U(VI) reduction were photogenerated electrons, superoxide radicals, and slightly reducing CO₂•⁻ intermediates of formic acid, as demonstrated by radical trapping experiments. Meanwhile, the optimized composite (B) also demonstrated exceptional structural stability and maintained approximately 78% of its initial activity after five consecutive cycles. Thus, the CeO₂/ZnO/MIL heterojunction is a promising visible-light photocatalyst for radionuclide remediation and offers a viable approach to the reduction of U(VI) and other redox-active radionuclides in an aqueous environment.

Keywords; Uranium remediation; Visible-light photocatalysis; Ternary heterojunction photocatalyst; NH₂-MIL-101(Fe); Charge transfer mechanism.

1. Introduction

The rapid development of the nuclear industry has led to an increased demand for uranium resources. Meanwhile, the environmental pollution resulting from uranium-containing wastewater has also been highly concerned[1]. Uranium is the primary fuel for nuclear power generation, due to its high energy density and critical relevance in the global energy sector[2]. However, aqueous effluents containing uranium species are generally generated by uranium mining, ore processing, fuel manufacture, nuclear power plants, and reprocessing of used nuclear fuel[3], [4]. In contrast, seawater contains approximately 4.5 billion tons of uranium-about 1000 times of the identified terrestrial reserves. However, the extremely low concentration ($\sim 3.3 \mu\text{g. L}^{-1}$) of uranium in seawater makes its large-scale exploitation economically unfeasible with current technologies. In addition, due to the radiotoxicity and chemical toxicity of uranium, the release of these radioactive wastewaters without adequate treatment poses a major hazard to the aquatic environment and human health[5]. Therefore, the development of effective, eco-friendly, and economically viable technologies for the removal and recovery of uranium from aqueous environments has been a significant research area in environmental remediation and nuclear chemistry[6]. Uranium mostly exists as the hexavalent uranyl ion (UO_2^{2+}) in oxidizing environmental conditions; besides, it has high aqueous solubility and mobility, it can quickly migrate through groundwater and surface water systems. In contrast, tetravalent uranium (U(IV)) has extremely low solubility and tends to precipitate as UO_2 or analogous solid phases[2], [7]. Thus, the reduction of soluble U(VI) to insoluble U(IV) has gained much attention, because it removes uranium from aqueous solutions and stabilizes it in a stable form appropriate for long-term storage or resource recovery[8].

In recent decades, enormous research efforts have been focused on the development of uranium removal and recovery techniques, including chemical precipitation, ion exchange, membrane separation, solvent extraction, adsorption, electrochemical treatment, and biological remediation[9], [10], [11], [12], [13], [14]. Under specific conditions, substantial removal efficiency can be achieved. However, many of these technologies suffer from limitations such as high operational costs, the production of secondary waste, difficult regeneration procedures, membrane fouling, poor selectivity, and partial immobilization of uranium[15]. Among these methods, adsorption has been the most studied since it is operationally simple and relatively low in energy usage. However, adsorption just transfers uranium from the liquid phase to the solid surface without changing the oxidation state and the possibility of further desorption and remobilization in the environment remains[16]. Therefore, technologies capable of simultaneously removing and stabilizing uranium are increasingly desirable. Recently, photocatalytic reduction has been regarded as one of the most promising technologies for uranium remediation because it couples solar energy consumption with the direct conversion of soluble U(VI) to insoluble U(IV)[17][18]. Particularly, in the presence of light irradiation, the electron-hole pairs are created in the semiconductor photocatalysts, and the photogenerated electrons decrease U(VI) to U(IV), and the holes are consumed by sacrificial agents or oxidizable species[19]. Interestingly, photocatalytic reduction has many advantages over conventional adsorption such as lower chemical consumption, secondary pollution, simultaneous uranium immobilization, recyclable catalyst, and use of renewable solar energy[20], [21]. However, the practical use of photocatalytic reduction remains constrained by the quick charge-carrier recombination, poor visible-light absorption, slow interfacial charge transfer, and limited stability of many of the typical semiconductor photocatalysts[19]. To the best of our knowledge, a number of semiconductor materials such as TiO_2 [22], ZnO [23], CdS [24], WO_3 [25], BiVO_4 [26], and $\text{g-C}_3\text{N}_4$ [27] and their heterojunctions have been investigated for the photocatalytic uranium and other radionuclides reduction. Although these photocatalysts have exhibited promising activity, many of them suffer from broad band gaps, photo corrosion, or inadequate

charge separation, therefore limiting their visible-light photocatalytic performance. Thus, great efforts have been made to design heterojunction photocatalysts for improving interfacial charge transfer and expanding the visible-light response[28].

In particular, metal-organic frameworks (MOFs) have attracted much attention as a class of photocatalytic materials due to their extraordinarily specific surface areas, tunable pore architectures, flexible electronic characteristics and abundant active sites[29]. Among these, NH₂-MIL-101(Fe) has gained increasing attention because of its outstanding visible-light absorption due to ligand-to-metal charge transfer, large pore volume, high adsorption capacity and comparatively simple production. Moreover, the amino functional groups enhance the visible-light harvesting and facilitate the charge transfer within the framework. However, the pristine NH₂-MIL-101(Fe) still suffers from low charge separation efficiency and quick recombination of photogenerated electron-hole pairs, which limit its photocatalytic reduction capability[28], [30], [31]. An efficient way to overcome these restrictions is the construction of semiconductor/MOF heterojunctions. ZnO has the characteristics of great electron mobility, high electrical conductivity and abundant surface-active sites, which promote the rapid transport of the photogenerated electron. However, its activity in visible light is limited by broad band gap and intense electron-hole recombination[32]. On the other hand, CeO₂ possesses a great oxygen storage capacity, numerous oxygen vacancies and reversible Ce³⁺/Ce⁴⁺ redox pair, which can assist charge trapping and electron migration[33]. Therefore, it is expected that the excellent visible-light harvesting capacity of the MOF, the efficient charge transport of ZnO and the electron-buffering property of CeO₂ are achieved through the integration of CeO₂ and ZnO with NH₂-MIL-101(Fe). Compared with traditional binary heterojunctions, ternary heterojunctions have numerous linked interfaces and complementary electronic structures, which can result in more effective charge separation and multichannel electron transport, while decreasing electron-hole recombination[34]. Furthermore, the improved performance is owed to cooperative interfacial contacts rather than the simple addition of three components, which may preserve more reduction-active electrons for the conversion of soluble U(VI) to less mobile U(IV), which provides a convincing mechanistic reason to develop ternary system CeO₂/ZnO/NH₂-MIL-101(Fe).[35] Therefore, the synergistic roles of CeO₂, ZnO and NH₂-MIL-101(Fe) in visible light-driven uranium reduction have not been thoroughly studied.

In this work, different CeO₂/ZnO/NH₂-MIL-101(Fe) heterojunction photocatalysts with varied oxide loadings were successfully synthesized via a one-step solvothermal method. The structural, morphological, optical and surface chemical properties of the prepared composites were systematically characterized by PXRD, FT-IR, SEM, TEM, XPS, UV-vis diffuse reflectance spectroscopy, photoluminescence spectroscopy, Mott-Schottky analysis and N₂ adsorption-desorption measurements. Their photocatalytic efficacy for visible-light-driven U(VI) reduction was comprehensively explored by studying the effects of catalyst dosage, initial uranium concentration, solution pH, sacrificial agent, and catalyst recyclability. Furthermore, the mechanism of the photocatalytic reduction was clarified by kinetic analysis, active-species trapping experiments, and band-structure analysis. This work presents an effective technique for building efficient MOF-based heterojunction photocatalysts for the removal of uranium as well as treatment of radioactive wastewater.

2. Experimental section

2.1 Materials and chemicals

Iron(III) chloride hexahydrate (FeCl₃·6H₂O), 2-aminoterephthalic acid (NH₂-BDC), N,N-dimethylformamide (DMF), ethanol (C₂H₅OH), cerium nitrate, zinc nitrate, sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), sodium perrhenate (NaReO₄, ≥99%, AR), and formic acid (HCOOH, 99%, AR) were

purchased from Shanghai McLean Biochemical Co., Ltd, and Chengdu Kelong Chemical Company, P. R. China. Other commercial chemicals were analytical grade and used without further purification.

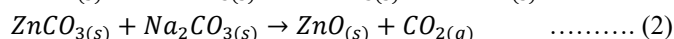
2.2 Catalysts preparation

Preparation of NH₂-MIL-101(Fe)

NH₂-MIL-101(Fe) was synthesized with some modifications according to an anterior reported solvothermal procedure[36]. Concisely, 1.3246 g FeCl₃·6 H₂O and 0.4492 g NH₂-BDC were added to 30 mL DMF and followed by ultrasonically dissolved for 30 min. The solution was transferred to an autoclave and heated at 110°C for 24 h, then cooled naturally. Finally, the obtained product was centrifuged, and acquired after three times rinsing with ethanol and DMF and vacuum drying at 60°C overnight.

Preparation of CeO₂, ZnO, and CeO₂/ZnO

CeO₂, ZnO, and CeO₂/ZnO were prepared following the reported procedure in the literature as in equation 1 and 2[37], [38] see (Supporting Information).



Preparation of CeO₂/NH₂-MIL-101(Fe)

CeO₂/NH₂-MIL-101(Fe) was solvothermal synthesized through a similar synthesis procedure of NH₂-MIL101(Fe). CeO₂ were dissolved in 10 ml DMF ultrasonically for 15 mins in a separate beaker, and was added during the course preparing NH₂-MIL-101(Fe). The remaining synthesis steps of CeO₂NH₂-MIL-101(Fe) were same as NH₂-MIL-101(Fe).

Preparation of ZnO/NH₂-MIL-101(Fe)

ZnO/NH₂-MIL-101(Fe) was solvothermal synthesized through a similar synthesis procedure of NH₂-MIL101(Fe). In which, ZnO were dissolved in 10 ml DMF ultrasonically for 15 mins in a separate beaker, and was added during the course preparing NH₂-MIL-101(Fe). The remaining synthesis steps of ZnO/NH₂-MIL-101(Fe) were same as NH₂-MIL-101(Fe).

Preparation of CeO₂/ZnO/NH₂-MIL-101(Fe) Composites

CeO₂/ZnO/NH₂-MIL-101(Fe) (A-C) were solvothermal synthesized through a similar synthesis procedure of NH₂-MIL101(Fe) as depicted in Figure 1. Initially, different quantities of CeO₂/ZnO either by adding fresh stock solution (10.8, 21.7, 43.5 ml) or (108, 216, 432 mg) during the course preparing NH₂-MIL-101(Fe) in 30 ml of DMF and sonicated for 15 min. The remaining synthesis steps of CeO₂/ZnO/NH₂-MIL-101(Fe) were same as NH₂-MIL-101(Fe). Finally, three different composites were obtained and named as; 2.5%CeO₂/5%ZnO/MIL (composite (A)), 5%CeO₂/10%ZnO/MIL (composite (B)), and 10%CeO₂/20%ZnO/MIL (composite (C)).

2.3 Catalysts characterization

X-ray diffraction (XRD) patterns of all samples were measured using a Cu radiation K_α (λ = 1.5418 Å, 40 kV, and 40 mA) (X'Pert PRO, PAN analytical Company, Holland). The alteration of functional groups was recorded by a Bruke TENSOR27 Fourier Transform Infrared Spectroscopy (FTIR). Thermogravimetric analysis (TG) was performed using a Q500 (TA instrument) in an air atmosphere. TG curves were obtained by heating in the range of 25°C to 800°C with a rate of 5°C min⁻¹. Photoluminescence spectra (PL) were recorded by a Hitachi F4600 fluoro spectrophotometer at the excitation of 310 nm under 500 V operating voltage. The UV-Vis diffuse reflectance spectra were recorded using the UNICO SQ-UV2802 with an

integrating sphere accessory. Microscopic morphologies were obtained on a Hitachi SU8100 Field-emission scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) data were acquired on the ThermoFisher Nexsa apparatus with an Al K α X-ray source. The binding energy (BE) was referenced to the C1s speak (284.8 eV). EPR spectra were recorded on an X-band Bruker EMX-10/12 spectrometer operating at RT. The EPR signals of N species in 30-GT were processed at a low temperature of 110 K.

2.4 Photocatalytic reduction experiments for U(VI)

In a 100 mL jacketed quartz beaker, 75 mL of U(VI) aqueous solution (20-40 mg/L) and 75 mg of photocatalyst were stirred for a while to disperse the photocatalyst uniformly. 1% HCOOH was added to the mixed solution, the pH was adjusted with 1 mol L⁻¹ NaOH and 1 mol L⁻¹ H₂SO₄ solution. To maintain the reaction temperature at 25 $\pm$ 1 $^{\circ}$ C, the jacketed beaker was connected with circulating water prior to photocatalytic reaction, and the mixed solution was consecutively stirred for 30 in darkness min in order to achieve U(VI) adsorption/desorption equilibrium. Photocatalytic reduction/removal experiments of U(VI) were conducted in air atmosphere under the simulated sunlight irradiation (a 300 W Xenon lamp) as well as under N₂. At specified time intervals, 3.0 mL of the reaction solution was collected and immediately filtered with 0.22 μ m nylon syringe filters to remove the photocatalyst. The concentration of soluble U(VI), Fe²⁺, Zn²⁺, and Ce⁺⁴ leaching in the filtrate liquid was measured by an inductively coupled plasma emission spectrometer (ICP-OES, Thermo Fisher ICAP7400). The samples were measured within 10 minutes of collecting and The U(VI) removal efficiency was calculated according to this equation [39] ;

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

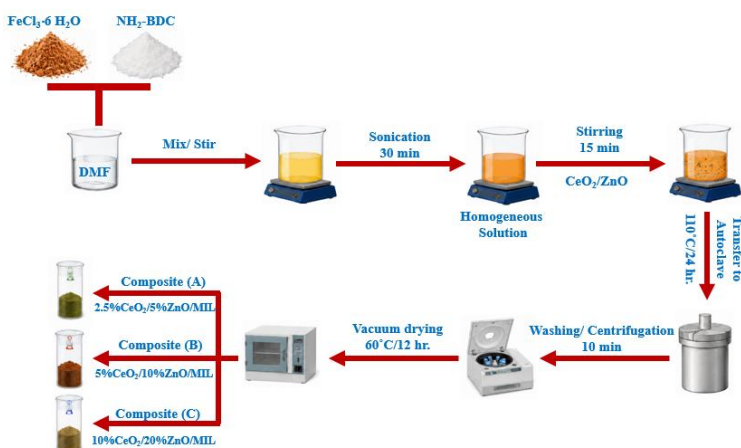


Figure 1. Schematic illustration of the solvothermal synthesis of CeO₂/ZnO/NH₂-MIL-101(Fe) composites

3. Results and discussion

The X-ray powder diffraction (PXRD) patterns of MIL, CeO₂/MIL, ZnO/MIL and CeO₂/ZnO/MIL (B) are shown in Figure 2a. The synthesized MIL sample exhibited the characteristic diffraction peaks of NH₂-MIL-101(Fe), especially in the low angle region ($2\theta = 8-11^{\circ}$), which confirms the formation of the MOF structure with high crystallinity, in agreement with previous literature [40]. The composite samples retain all the major distinctive diffraction peaks of MIL after addition of CeO₂ and ZnO, suggesting that the crystalline structure is maintained over the whole composite synthesis process, which indicates that the inclusion of metal oxides does not alter the structural stability of the pure MIL. Besides the MIL reflections, numerous more diffraction peaks were detected in the composite materials which could be attributed to the

crystalline phases of CeO₂ and ZnO. In specific, the characteristic reflections detected at $2\theta \approx 28.5^\circ, 33.1^\circ, 47.5^\circ$ and 56.3° for CeO₂/MIL correspond to the cubic fluorite structure of CeO₂. While ZnO/MIL displayed characteristic peaks at $\sim 31.7^\circ, 34.4^\circ, 63.5^\circ$ and 69.3° corresponding to the hexagonal wurtzite phase of ZnO[41], [42]. The diffraction peaks of CeO₂ and ZnO can be observed in the composite (B), and typical aforementioned reflections of MIL were also existed, which confirms the successful synthesis of the ternary heterostructure. Compared to pristine MIL, the composite samples exhibit slight shifts in the peak intensity and slight broadening of the peaks which could be attributed to the interaction of the oxide nanoparticles with the MOF framework and the partial occupying of the pore channels by the deposited metal oxides. However, no other impurity phases are identified which is indicative of the high purity of produced composite. Furthermore, the main MIL reflections were still observable after the addition of oxide showing that the metal oxides are predominantly dispersed on the surface and inside the pore network of the framework rather than replacing Fe coordination sites in the crystal lattice.

FT-IR spectra of MIL, CeO₂/MIL, ZnO/MIL and CeO₂/ZnO/MIL were recorded to study the chemical bonding environment and validate the successful incorporation of the metal oxides into the MIL framework. As shown in Figure 2b. All samples exhibited very comparable spectral features, which indicates that the composite created retained the core framework structure of NH₂-MIL-101(Fe). The broad absorption bands in the region of 3460-3330 cm⁻¹ are attributed to the stretching vibrations of the N-H groups in amino-functionalized organic linker, whereas the band around 1620 cm⁻¹ is attributed to the N-H bending vibration. The characteristic asymmetric and symmetric stretching vibrations of the coordinated carboxylate groups (–COO⁻) were observed at about 1570-1560 cm⁻¹ and 1390-1380 cm⁻¹, respectively, which confirm the coordination of the NH₂-BDC ligand to the Fe centers in the framework. Furthermore, the absorption band at 1250-1260 cm⁻¹ is due to the stretching vibration of C–N of the amino group and the peak at 750 cm⁻¹ is assigned to the C–H bending vibration of the aromatic benzene ring. The composite materials exhibited several more absorption bands at the low frequency range. weak bands in the area of 520-540 cm⁻¹ and 430-470 cm⁻¹ which might be ascribed to the Ce–O and Zn–O stretching vibrations in CeO₂/MIL and ZnO/MIL respectively. Notably, the composite (B) exhibited absorption bands of Ce–O and Zn–O, indicating the effective integration of both metal oxides into the MOF framework. However, no evident significant alteration or depletion of the characteristic MIL peaks was detected following the oxide loading, suggesting that the chemical bonding environment of the MIL framework was preserved after the incorporation of CeO₂ and ZnO. The existence of all essential characteristic bands supports the integrity of the crystalline framework during the composite synthesis, and the appearance of metal-oxygen vibrations confirms the successful assembly of the CeO₂/ZnO/MIL heterostructure.

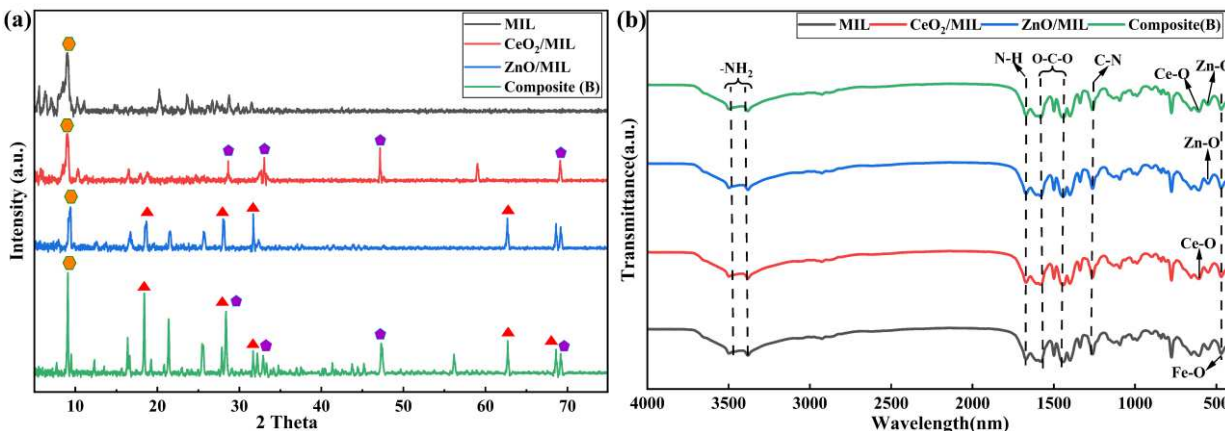


Figure 2. (a) XRD patterns of the MIL, CeO₂/MIL, ZnO/MIL, and Composite (B), (b) FT-IR of MIL, CeO₂/MIL, ZnO/MIL, and Composite (B).

The morphology of the MIL and composite (B) was examined by scanning electron microscope SEM-EDS. Where the MIL showed a regular octahedral morphology as depicted in Figure 3a. Interestingly, when CeO₂/ZnO were introduced to the MIL to synthesize the composite (B), the morphology did not undergo significant changes and retained its octahedral structure, as shown in Figure 3b. In addition, thermogravimetric analysis (TGA) studies of the MIL and Composite (B) were conducted to determine the thermal stability and the decomposition behavior as shown in Figure S1. To explore, both materials displayed a minor initial weight loss below ~150 °C, which is ascribed to the elimination of physically adsorbed water and remaining solvent molecules inside the porous structure. The pristine MIL showed a significant weight loss in the range of 300-500 °C owing to the degradation of organic linkers and the collapse of MOF framework. In contrast, Composite (B) showed a retarded disintegration process and higher residual weight (~55% at 800 °C) than MIL (~40%), demonstrating the improved thermal stability following addition of CeO₂ and ZnO. This could be attributed to the strong interaction between metal oxides and the NH₂-MIL-101(Fe) framework, where the inorganic components serve as thermally stable supporting phases, leading to an enhanced structural integrity of the composite.

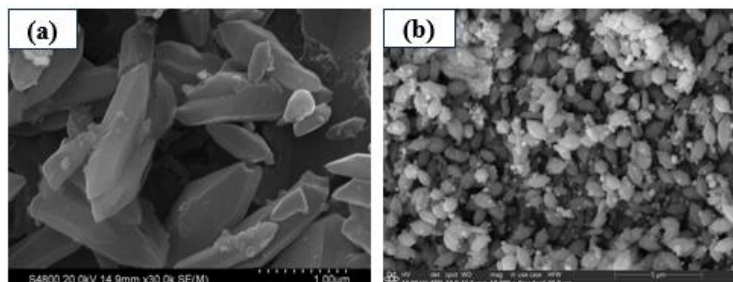


Figure 3. SEM images for MIL (a), Composite (B) (b)

The photocatalysts were further structurally characterized by N₂ adsorption-desorption analysis, and the corresponding isotherms of MIL and composite (B). Both materials show Type I adsorption-desorption isotherms, which confirm the typical microporous structure of the MIL framework is retained after the introduction of CeO₂ and ZnO. Both samples exhibited a significant increase of N₂ uptake at low relative pressures $P/P_0 < 0.1$, a typical feature of microporous materials, suggesting the presence of a large concentration of accessible micropores within the framework. As shown in Figure 4a, the N₂ adsorption capacity of the composite (B) is substantially decreased over the whole range of relative pressure compared with pristine MIL, demonstrating that the specific surface area and pore volume decreased following the incorporation of the oxides. This decrease might be owing to the partial occupation or blocking of the microporous channels by CeO₂ and ZnO nanoparticles and an increase in the framework density due to heterostructure development. Meanwhile, the composite (B) showed relatively good adsorption capacity as shown in Figure 4b, indicating that a considerable amount of the porous framework is still accessible, providing sufficient active sites for photocatalytic reactions. Furthermore, the slight increase in the adsorption at higher relative pressures could be an indication of the presence of additional interparticle voids or mesoporous structures generated during the production of the composite (B), which could facilitate the mass transport and reduce the diffusion resistance in the catalyst. Thus, the inclusion of CeO₂ and ZnO slightly reduces the textural properties of the pristine MIL, nevertheless, the composite (B) was still maintained a highly porous structure and demonstrates enhanced charge transfer characteristics. The maintained porosity with effective diffusion of reactants and improved charge separation provides the

favorable conditions for the adsorption and photocatalytic reduction of U(VI), resulting in a good photocatalytic performance of the composite material. On the one hand, the specific surface area, pore volume and average pore diameter of the two materials are presented in Table 1. To explore, the addition of CeO₂/ZnO compared with pure MIL results in a reduction in the specific surface area. However, composite (B) showed a smaller microporous volume comparing to MIL, whereas the average pore diameter was increased. This variation might be attributable to the crystal inclusion and distortion induced by the oxides loading, and the enhancement of mesopore formation by interparticle packing. Even though, the specific surface area of CeO₂/ZnO/MIL is slightly reduced, it remains as ~1071 m²/g, offering sufficient active sites for photocatalytic reactions. Moreover, increasing the average pore size can significantly minimize the diffusion resistance of U(VI) in the pores, which creates favorable conditions for consequent photocatalytic reactions.

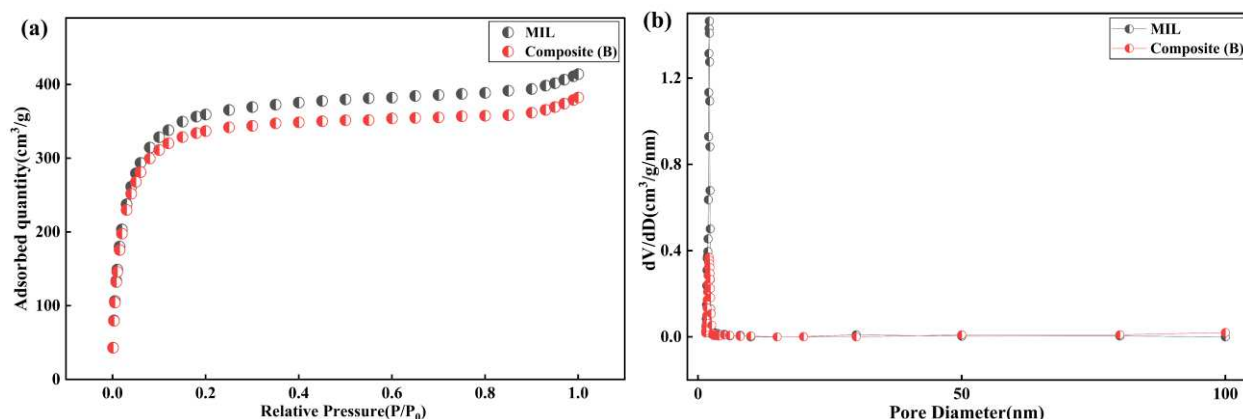


Figure 4. (a) N₂ adsorption-desorption isotherms of MIL and Composite (B), (b) BJH pore size distribution diagrams of MIL and Composite (B)

Table 1 specific surface area, pore volume and average pore diameter of MIL and composite (B)

Sample	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
MIL	1213.9	0.645	2.12
CeO ₂ /ZnO/MIL(B)	1071.343	0.5821	2.1345

3.2 Optical and electronic properties

The ultraviolet-visible diffuse reflectance spectra of the samples were determined by ultraviolet-visible diffuse reflectance spectroscopy (UV-vis-DRS), as shown in Figure S2, since the photocatalytic activity of the catalyst depends on the optical response characteristics[43]. The absorption edge of the CeO₂/ZnO/MIL is slightly red shifted compared to the MIL. Composite (B) demonstrated that the introduction of metal oxide has a beneficial effect on the enhancement of the visible light utilization efficiency. On one hand, the bandgap (E_g) of the MIL and three composites (A, B and C) can also be calculated according to Kubelka-Munk equation [44]; $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where A is a constant, $h\nu$ is the photon energy, E_g is the bandgap, and α is the absorption coefficient. As reported, when n equal to 1, it means, the material is an in direct bandgap semiconductor, while, when n equal to 4 it means the material is an in-direct bandgap semiconductor[45]. The bandgap energy of the MIL and the three composites were indirectly calculated from the intercept of the tangent of $(\alpha h\nu)^2$ with the photon energy as shown in Figure 5a, which were approximately 2.71 eV, 2.61 eV, 2.66 eV and 2.55 eV, respectively. For further investigation of the band structure of the materials, the flat band potential (V_{FB}) of MIL and composite (B) was determined from the

Mott-Schottky curves as -0.59V and -0.64V (vs. Ag/AgCl), respectively as presented in Figure 5b. Moreover, the Mott-Schottky plots of MIL and composite (B) exhibited a positive slope, indicating their n-type semiconductor behavior. The possible conversion between Ag/AgCl electrode and the standard hydrogen electrode suggests the V_{FB} values of MIL and composite (B) are -0.39V and -0.44V (vs. NHE) respectively. Moreover, the CB potential of n-type semiconductor is 0.1V lower than V_{FB} [45], the CB potentials of MIL and composite (B) are predicted to be -0.49V and -0.54V (vs. NHE), respectively. Thus, the valence band (VB) potentials of MIL and composite (B) were calculated as +2.22V and +2.12V, respectively, based on the formula $E_g = E_{VB} - E_{CB}$.

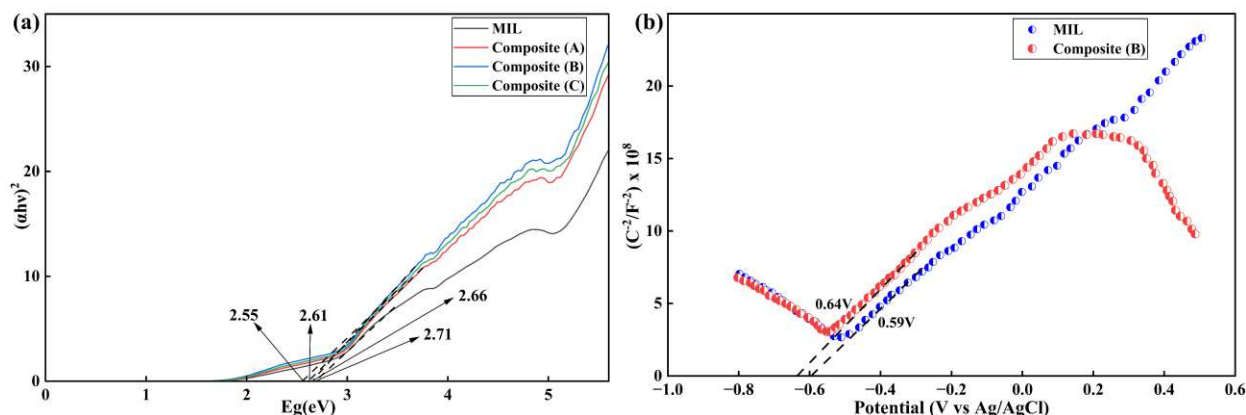


Figure 5. (a) Tauc plots; (b) Mott-Schottky curves of MIL and Composite (B).

The photocatalytic reduction performance

The photocatalytic reduction efficacy of NH_2 -MIL-101(Fe), referred to as (MIL), and $CeO_2/ZnO/NH_2$ -MIL-101(Fe) composites containing different oxide loadings (composite (A), composite (B), and composite (C) corresponding to 2.5% CeO_2 /5% ZnO /MIL, 5% CeO_2 /10% ZnO /MIL, and 10% CeO_2 /20% ZnO /MIL respectively) were investigated for the reduction of U(VI) under visible light irradiation, as illustrated in Figure 6a. Following the attainment of adsorption-desorption equilibrium during a 30-minute dark interval, the results indicated that the adsorption during this dark phase can be disregarded, corroborating that U(VI), is not efficiently adsorbed onto sediment and mineral surfaces; the subsequent reduction in U(VI) concentration is primarily due to photocatalytic activity. Upon exposure to visible light, all catalysts demonstrated a time-dependent reduction response after 60 minutes of irradiation, with the unmodified MIL displaying the least efficacy, achieving removal efficiencies of approximately 43.7% in air and around 49% in nitrogen. Conversely, all CeO_2/ZnO synergistic composites shown a significant increase in photocatalytic performance attributed to the synergistic effects of heterojunction formation and improved interfacial charge transfer. Specifically, composite (A) exhibited moderate efficiencies of approximately 72% in air and 77% in nitrogen, whereas composite (C) showed further improved to around 79% in air and 82% in nitrogen, indicating that oxide loading optimizes visible-light efficiency to a certain extent. Notably, composite (B) exhibited the highest photocatalytic efficiency of 92.9% in an air atmosphere and 95.1% in the nitrogen environment as presented in Table S1. The slightly enhanced efficiency in N_2 compared to air further corroborates the impact of dissolved oxygen competition on the suppression of electron transfer to U(VI) reduction. This sequential arrangement of activities (MIL < A < C < B) distinctly underscores the importance of the optimal loading ratio of CeO_2/ZnO for maximizing photocatalytic reduction efficiency by adjusting light absorption, charge transport, and interfacial redox processes. Additionally, some literature on U(VI) reduction is listed for comparison in Table 2.

Along this line, Figure 6b exhibited the photocatalytic reduction performance of 75 mg CeO₂/MIL, ZnO/MIL, and optimized composite (B) with 20 mg/L of U(VI) in air and N₂ atmospheres. All catalysts showed a rapid decrease in U(VI) concentration upon visible-light irradiation within 60 min, with adsorption-desorption equilibrium attained after 30 min in darkness, indicating photocatalysis induced the reduction process. The composite (B) showed the highest photocatalytic activity in both atmospheres, with 92.9% and 95.1% U(VI) removal efficiencies in air and N₂, respectively. 10%ZnO/MIL reached 83.1% and ~85.2%, while 10%CeO₂/MIL achieved 74.6% and 79.3% under air and N₂, respectively within 60 min under light. In particular, all catalysts reduced more efficiently in nitrogen than air, which can be ascribed to the removal of dissolved oxygen, a competitive electron acceptor, allows more photogenerated electrons to directly reduce U(VI). ZnO/MIL showed better activity than CeO₂/MIL, suggesting it can improve electron transport and visible-light consumption. Interestingly, combining both metal oxides in the MOF created a cooperative heterojunction, enhancing the optimized composite B's photocatalytic reduction capability, charge transfer, and electron availability for U(VI) reduction. These results indicate that the CeO₂/ZnO/NH₂-MIL-101(Fe) ternary heterostructure is more effective than adding single oxides CeO₂ or ZnO.

Table 2 Photocatalytic reduction efficiency of the previous studies

Photocatalyst	U(VI) removal %	Removal Time (min)	pH	Initial U(VI) mg. L ⁻¹	Ref
NH ₂ -MIL-125(Ti) Facet-engineered	> 97	20	Broad scale≈7	100	[46]
MIL-53(Fe)	80	120	5	50	[47]
NH ₂ -MIL-125(Ti)@TpPa-1 (MOF/COF)	~95	-	5	50	[48]
Phosphate-defect NH ₂ -MIL-53(Fe) (defect-engineered MOF)	99.8	-	5	50	[49]
CeO ₂ /ZnO/ NH ₂ -MIL-101(Fe)	95.1	60	5	20	This work

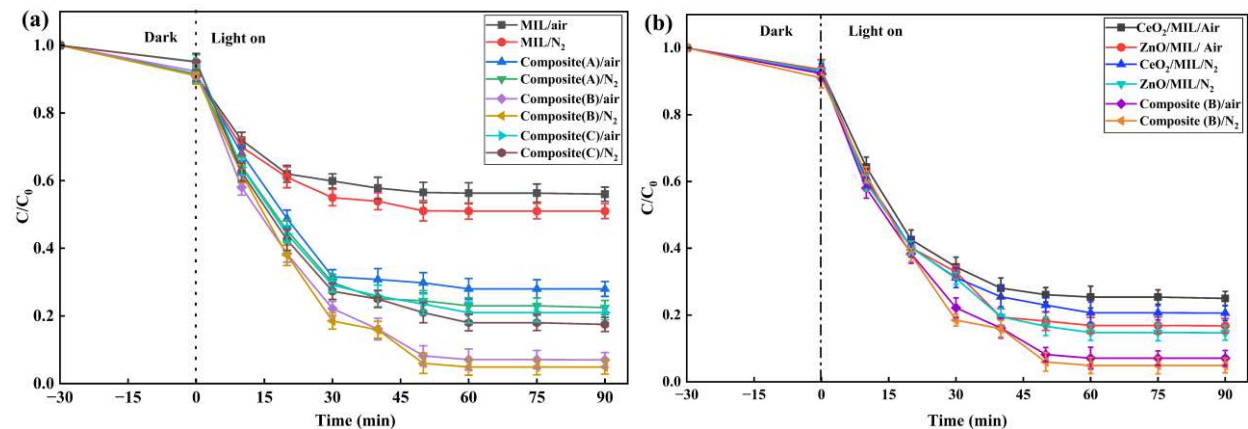


Figure 6. (a) Reduction efficiency of U(VI) by MIL and composite (A-C); (b) Reduction efficiency of U(VI) by MIL, CeO₂/MIL, ZnO/MIL, and composite (B)

As presented in Figure 7a and Figure S3, the reduction of U(VI) follows the pseudo-first-order kinetics (FPO), ($\ln[C_0/C_t] = -kt$) [50]. The calculated rate constants (k) and R^2 for the reduction of U(VI) by each

catalyst were illustrated, where composite (B) exhibits the fastest reduction rate, compared to MIL and the other two composites. In contrast, the pseudo-second-order kinetics (PSO) was also calculated and presented in Figure S4 and Table 3, confirming that the reaction followed the FSO kinetics.

Effect of pH on photocatalytic U(VI) reduction

The pH of the solution is an important factor for the photocatalytic reduction of U(VI), since it can influence the uranium speciation, the surface charge characteristics of photocatalyst, the adsorption behavior and the interfacial electron-transfer processes simultaneously[51]. It can be shown from Figure 7b that the photocatalytic reduction efficiency of composite (B) was highly pH dependent. The U(VI) removal efficiency was dramatically raised from 57.0% to 95.1% with the increase of pH from 3 to 5, suggesting that the mildly acidic conditions are ideal for uranium photoreduction in agreement with literature[52]. To illustrate, under strongly acidic conditions (pH = 3), the relatively lower photocatalytic efficiency could be attributed to the excessive proton competition with uranyl ions for the adsorption sites on the catalyst surface. In which, the excess of H⁺ ions can be adsorbed by oxygen-containing functional groups such as carboxylate oxygen, hydroxyl groups, and surface sites of Ce-O/Zn-O, which results in the reduction of the effective interaction of UO₂²⁺ with the photocatalyst. Also, the high proton concentration may also boost the recombination of electrons and holes and limiting the availability of photogenerated electrons for the reduction of uranium. Particularly, the photocatalytic activity was significantly improved with the increase of pH to 5. In this state, U(VI) predominantly occurs as hydrated uranyl ions (UO₂²⁺) and may be efficiently adsorbed on the NH₂-MIL-101(Fe) framework through coordination interactions with amino groups, carboxylate oxygen atoms and Fe-O clusters. Meanwhile, the oxygen vacancies and surface hydroxyl groups of CeO₂ can serve as extra adsorption sites for the enrichment of U(VI) species at the semiconductor/MIL interfaces. The advantageous adsorption configuration is conducive to quick electron transfer from the photoexcited composite to the adsorbed uranium species as in equation 3. On the other hand, photocatalytic efficiency was lowered steadily further increase of pH from 5 to 8. The removal efficiency was lowered from 95.1% at pH 5 to 31.0% at pH 8. This reduction could be ascribed to the hydrolysis of uranyl ions and the creation of other hydrolyzed uranium species such as UO₂OH⁺ and (UO₂)₂(OH)₂²⁺, which may lead to uranium hydroxide precipitates. These species interact less strongly with the active sites and likely impede effective interfacial electron transport. Furthermore, at higher pH values, the formation of carbonate complexes may limit the availability of free uranyl ions for photocatalytic reduction.

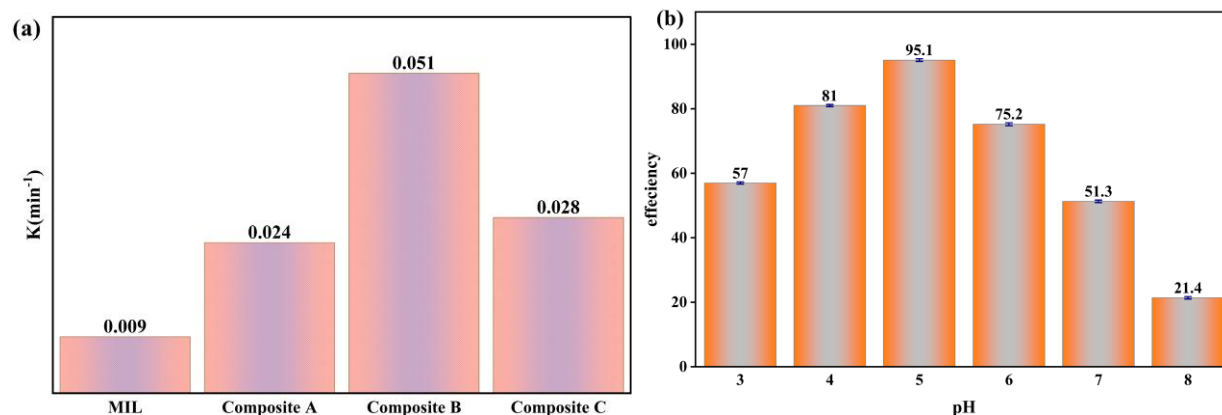
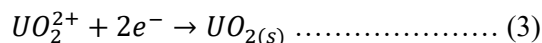


Figure 7. (a) first-order kinetic curve for photocatalytic performance of MIL and composite (A-C); (b) Reduction efficiency of U(VI) at different pH values.

Control studies were conducted under identical conditions to identify the contributions of photolysis, adsorption and photocatalysis using 20 mg L⁻¹ U(VI), 75 mg of photocatalyst and 1% (v/v) HCOOH as sacrificial agent as depicted in Figure 8a. In the absence of the photocatalyst, the U(VI) concentration remained almost unchanged over the whole reaction time, indicating that light alone was insufficient to produce considerable U(VI) reduction. Similarly, in the presence of the catalyst alone, only minor U(VI) concentration changes (~9-12%) were observed after the dark period, indicating that adsorption is a minor contributor to the overall removal process. On the other hand, when composite (B) was used in the presence of 1% HCOOH, a fast drop of U(VI) concentration was observed upon visible-light irradiation. In 60 mins, 95.1% removal efficiency of U(VI) was achieved, indicating that the presence of HCOOH, composite (B), and light irradiation are responsible of photocatalytic reduction of U(VI) to U(IV). In which, the presence of 1 vol% HCOOH further promotes the reduction process, which successfully scavenge the photogenerated holes, decreasing the electron-hole recombination, and prolonging the lifetime of photogenerated electrons accessible for U(VI) reduction. Therefore, the chance of electron transfer to reduce U(VI) species is much raised, resulting in the improved photocatalytic reduction efficiency.

Table 3 The FPO and PSO calculations

Catalyst	FPO		PSO	
	K (min ⁻¹)	R ²	K (min ⁻¹)	R ²
MIL	0.0063	0.922	0.0127	0.933
Composite A	0.0211	0.913	0.0682	0.939
Composite B	0.0533	0.985	0.1417	0.936
Composite C	0.0248	0.977	0.0796	0.970

The effect of the catalyst dosage

Figure 8b showed the photocatalytic reduction of U(VI) by the Composite (B) photocatalyst under visible-light irradiation using 25, 50, and 75 mg of catalyst in 100 mL of 20 mg L⁻¹ U(VI) solution containing 1 vol% HCOOH. All suspensions were magnetically stirred in darkness for 30 min before illumination until adsorption-desorption equilibrium was reached. The results showed that the efficiency of photocatalytic reduction increased gradually with increase of catalyst dosage. The 75 mg catalyst loading was the most active of the tested catalyst loadings, resulting in about 95.1% U(VI) reduction in 60 min after which the reaction achieved equilibrium. In contrast, the reduction efficiencies obtained with the catalyst loading of 50 mg and 25 mg were significantly lower, reaching about 82% and 57%, respectively, under the identical reaction conditions. The enhanced photocatalytic activity with higher catalyst loading could be attributed to the increased number of active sites available for U(VI) adsorption and reduction and the enhanced production of photogenerated charge carriers under visible-light irradiation. Moreover, the increase in catalyst dose leads to a larger effective contact area between photocatalyst surface and aqueous U(VI) species, which facilitate the surface adsorption and promotes the interfacial electron transfer from photocatalyst to reduce uranyl ions.

The effect of initial U(VI) concentration

The effect of initial U(VI) concentration on the photocatalytic reduction activity of Composite (B) was investigated using 20, 30, and 40 mg L⁻¹ U(VI) solutions as shown in Figure 9a. The experiments were performed under visible-light irradiation with 75 mg photocatalyst suspended in 100 mL U(VI) solution containing 1 vol% HCOOH after 30 min dark adsorption to reach adsorption-desorption equilibrium. The

results clearly showed the obvious effect of initial U(VI) concentration on the effectiveness of photocatalytic reduction. To illustrate, the 20 mg L⁻¹ U(VI) solution displayed the best photocatalytic activity among the tested doses of 95.1% in 60 min under visible-light irradiation. Conversely, increasing the initial U(VI) concentration to 30 mg L⁻¹ reduced the final reduction efficiency to about 63%, and increasing it further to 40 mg L⁻¹ led to only 38% reduction under identical reaction conditions. The excellent photocatalytic activity could be ascribed to the larger ratio of accessible active sites and photogenerated electrons to the amount of U(VI) ions in solution at the lower initial U(VI) concentration. Under these conditions, the surface of the composite (B) possesses abundant adsorption sites for the effective adsorption of uranyl ions and quick interfacial electron transfer, which promotes the reduction of U(VI) to U(IV). In addition, visible-light irradiation produced sufficient photogenerated electrons to reduce most of the adsorbed U(VI) species, and 1 vol% HCOOH effectively trapped the photogenerated holes, suppressing electron-hole recombination and prolonging the lifetime of reactive electrons. On the other hand, higher initial concentrations of U(VI) lead to a great number of uranyl ions competing for the same catalyst surface and the same number of photogenerated electrons. As a result, active sites are gradually saturated and the electron/U(VI) ratio falls, therefore hindering the reduction ability of the photocatalyst. Furthermore, a rise in the concentration of dissolved U(VI) leads to increased possibility of mass transfer constraints and limits the diffusion of U(VI) species towards the catalyst surface and consequently hinders the overall photocatalytic reduction process.

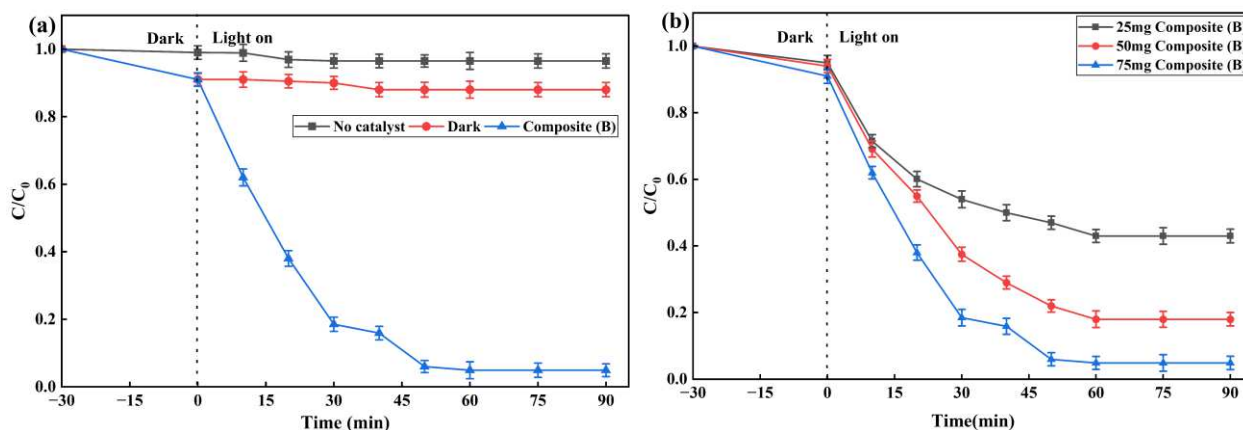


Figure 8. (a) Reduction efficiency of U(VI) by Composite (B) under light/dark conditions and under visible light only; (b) Effect of composite (B) dosage on U(VI) reduction efficiency.

The effect of HCOOH concentration

As shown in Figure 9b, the photocatalytic reduction of U(VI) using Composite (B) with 0, 0.1, 0.5, 1.0 and 2.0 vol% HCOOH under visible light irradiation showed the effect of formic acid concentration. The experiments were performed by using 75 mg of Composite (B) in 100 mL of 20 mg L⁻¹ U(VI) solution, after 30 min dark adsorption and visible-light irradiation. In the absence of HCOOH, only a small decrease of U(VI) concentration was observed with the final removal of 15%. Similarly, the addition of 0.1 vol% HCOOH showed a slight improvement with a final elimination of around 21%. Obviously, the photocatalytic process was improved by increasing the concentration of HCOOH to 0.5 vol% to about 51% U(VI) elimination efficiency. On the one hand, the maximum photocatalytic activity of about 95.1% was obtained at 1.0 vol% HCOOH. However, the final removal efficiency dropped to around 79% when the HCOOH concentration increased to 2.0 vol%, suggesting that the excessive formic acid does not further accelerate the process. To illustrate, the positive effect of HCOOH is mainly related to its role as a sacrificial

hole scavenger. The presence of HCOOH under visible-light irradiation consumes the photogenerated holes, thus suppressing electron-hole recombination, increasing the lifetime and availability of photogenerated electrons for the reduction of adsorbed U(VI) species. At low concentrations of HCOOH the hole scavenging is not sufficient and a large fraction of the photogenerated electrons recombines before entering the reduction reaction. In contrast, 1.0 vol% HCOOH offers a good compromise between quick hole consumption and efficient electron utilization. The performance drops at 2.0 vol% HCOOH could be due to over-adsorption of formate species on the catalyst surface, which may compete with U(VI) for the active sites, and thereby partially block the interfacial electron transfer.

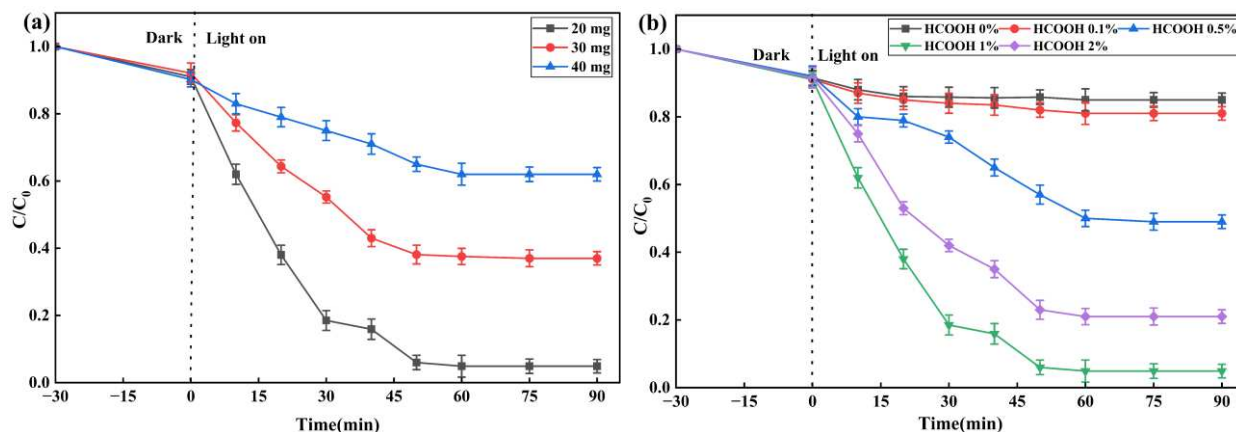


Figure 9. (a) Effect of U(VI) concentration on reduction efficiency; (b) Effect of HCOOH dosage on U(VI) reduction efficiency.

The effect of different organic additives

Figure 10a showed the effect of several organic additions on the visible-light photocatalytic reduction of U(VI) by Composite (B) using 1 vol% formic acid (HCOOH), methanol (CH₃OH) and ethanol (CH₃CH₂OH) as sacrificial agents. The experiments were performed at pH 5 using 75 mg of composite (B) photocatalyst and distributed in 100 mL of 20 mg L⁻¹ U(VI) solution after 30 min dark adsorption before irradiation with visible light. The results clearly indicate that the type of the organic component has a strong influence on the efficacy of the U(VI) photocatalytic reduction. In which, the additive with the highest photocatalytic activity was HCOOH, which rapidly reduced the U(VI) concentration after light irradiation to achieve 95.1% of removal in 60 minutes. This improvement in the performance of HCOOH is due to its excellent hole scavenging ability. Under the irradiation of visible light, HCOOH is easily oxidized by the photogenerated holes, which can effectively inhibit the recombination of electrons and holes and prolong the lifetime of electrons in conduction band. In addition, the oxidation of formic acid produces highly reducing intermediates like the CO₂[•] radical, which can further contribute to the reduction of U(VI) and thus improve the overall photocatalytic process. This results in more photogenerated electrons available for the conversion of soluble U(VI) to insoluble U(IV). On the other hand, the use of CH₃OH resulted in much reduced reduction efficiency of 35% of U(VI) removal. An even lower photocatalytic activity of 28% was observed under the same reaction conditions when ethanol was used. To illustrate, methanol and ethanol can also act as sacrificial hole scavengers, however their oxidation occurs via several intermediate processes, including the generation of alkoxy radicals and aldehydes, leading to slower hole consumption and less effective usage of photogenerated electrons. In addition, oxidation intermediates of alcohols could compete with U(VI) for surface active sites, or partially block catalytic sites, thereby reducing the efficiency of interfacial electron transfer.

Recyclability of Composite (B)

The five successive photocatalytic reduction cycles were carried out in N_2 environment to investigate the practical application and long-term stability of the optimized composite (B) photocatalyst, and the results are shown in Figure 10b. Obviously, the catalyst showed excellent photocatalytic activity in recycling experiments; however, a slight decrease in the reduction efficiency was noted with increasing the number of cycles. As aforementioned, composite (B) showed reduction efficiencies of 95.1% in N_2 atmosphere in the first cycle. After five continuous cycles, the reduction efficiencies were still about 78%, indicating that the catalyst maintained a large part of its initial activity. The relatively small decrease in the performance could be ascribed to the partial accumulation of active sites by strong adsorption reaction intermediates or products, slight loss of catalyst during the recovery or washing processes, and progressive surface deactivation during the repeated photocatalytic reactions. Nevertheless, the activity slightly decreases after five cycles, suggests that the composite (B) has a good structural stability and recyclability. To further check the stability of the photocatalyst, FT-IR and PXRD tests were performed after the five cycling experiments (Figure S5,6). It was worth noting, the characteristic functional-group vibrations and diffraction peaks were basically remained unchanged after five cycles, suggesting that the chemical structure and crystallinity of the composite (B) were well maintained during the photocatalytic process. Additional confirmation of leaching for Fe^{+3} , Zn^{+2} , and CeO_2 was carried out by ICP-OES, the leaching percentage results showed that negligible amounts for the measured ion were measured as in Table S2, which verified that the optimized composite has owing durability, structural robustness, and reusability, indicating its considerable potential for practical applications for the photocatalytic reduction of U(VI)-contaminated aquatic systems.

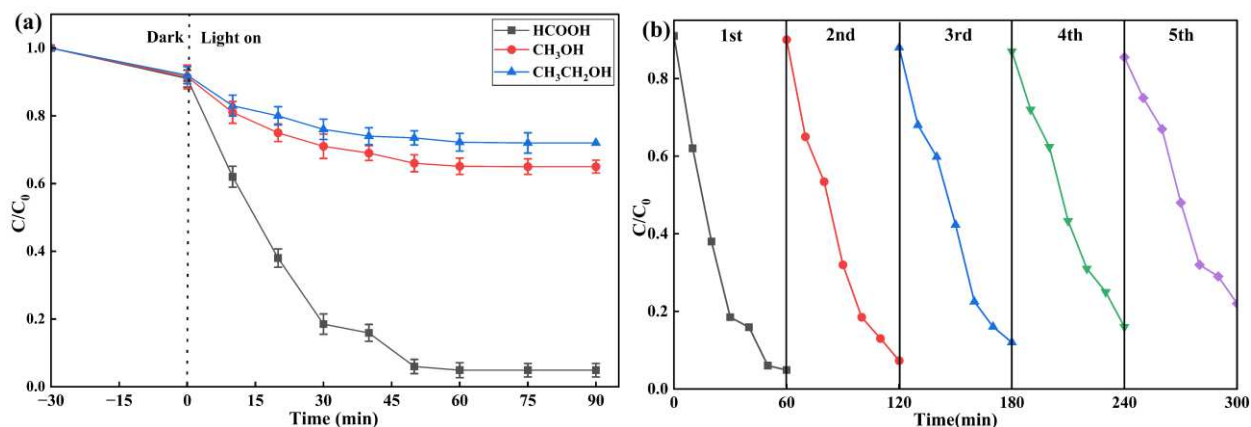


Figure 10. sacrificial organic additives for U(VI) reduction; (b) Cyclic test of composite (B) for U(VI) reduction.

To further explore the separation and recombination behavior of photogenerated charge carriers, photoluminescence (PL) spectra of MIL, composite (A), composite (B), and composite (C) were recorded. It is known that PL emission intensity is directly proportional to the recombination probability of photogenerated electron-hole pairs; thus, a lower PL intensity normally suggests a more efficient charge separation and migration. In Figure S7, the highest emission peak with the central wavelength was displayed for the pristine MIL, indicating the high recombination rate of the photogenerated charge carriers in the MIL framework. After the introduction of CeO_2 and ZnO , the PL intensity decreased remarkably for all composite samples, which verified that the formation of the $CeO_2/ZnO/MIL$ heterojunction efficiently suppressed the electron-hole recombination and enhanced the interfacial charge transfer. Among the analyzed samples, composite (B) displayed the lowest PL emission intensity, indicating the most effective separation and migration of photoexcited electrons and holes. This result is in good agreement with our

photocatalytic reduction experiments where the composite (B) exhibited the best U(VI) reduction efficiencies of about 92.9% and 95.1% under air and N₂ atmospheres, respectively. On the other hand, composite (A) and composite (C) exhibited intermediate PL intensities, which suggests that the incorporation of metal oxides improved the charge separation, compared to pristine MIL; however, the heterojunction effect was not as efficient as that of the optimized composite (B) composition. Therefore, the enhanced performance of composite (B) could be ascribed to the optimum loading of CeO₂ and ZnO, which are responsible for providing effective charge-transfer pathways, thereby, facilitating the migration of photogenerated electrons toward surface-active sites while suppressing charge-carrier recombination.

Further investigation of the interfacial charge transfer process of MIL and the related Nyquist plots for composite (A), composite (B), and composite (C), electrochemical impedance spectroscopy (EIS) was carried out. In general, the diameter of the semicircular arc in the Nyquist plot is directly related to the CeO₂/ZnO/MIL (B) charge-transfer (R_{ct}) at the electrode/electrolyte interface, where a smaller arc radius corresponds to the smaller charge-transfer resistance, faster interfacial electron migration, and more efficient separation of photogenerated charge carriers[53]. As illustrated in Figure 11, the greatest semicircular arc of pure MIL indicated the highest charge-transfer resistance and the slowest electron-transport kinetics. Meanwhile, the incorporation of CeO₂ and ZnO efficiently decreased the arc radius, which verified the formation of CeO₂/ZnO/MIL heterojunction efficiently promoted charge migration and inhibited charge recombination. Among all the samples studied, composite (B) exhibited the lowest semicircle diameter, which means the lowest resistance to charge transfer and the most effective electron transfer mechanism at the interface. s

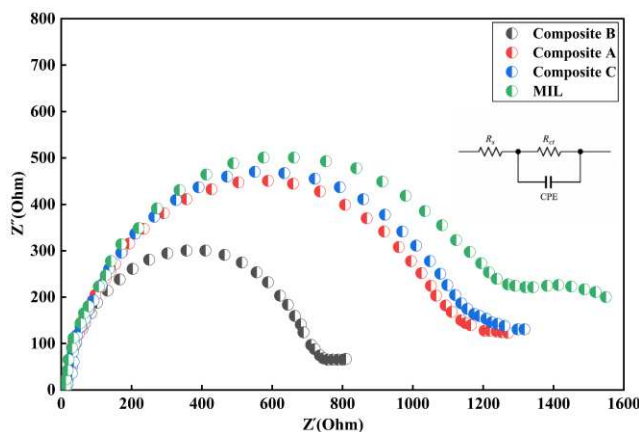
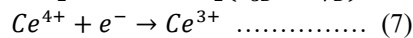
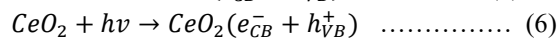
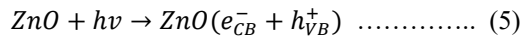
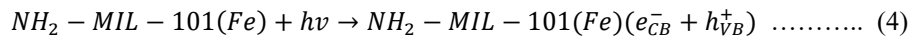


Figure 11. EIS diagram For MIL and composites A-C.

X-ray photoelectron spectroscopy (XPS) was carried out to investigate the elemental composition, surface chemical states, and electronic interactions of MIL, CeO₂/MIL, ZnO/MIL, and CeO₂/ZnO/MIL composites. The corresponding spectra are presented in Figure 12. The survey spectra showed the existence of C 1s, N 1s, O 1s, and Fe 2p elements in MIL, additional signals of Ce 3d, Zn 2p, and U 4f elements were identified, respectively as in Figure 12a, confirming the effective inclusion of the metal oxides in the MOF framework. In Figure 12b C 1s spectra, the three typical peaks at ~283.2, 284.6, and 287.4 eV could be attributed to C-C/C=C, C-N, and O-C=O bonds, respectively, resulting from the NH₂-BDC organic linker. Figure 12c showed the N 1s spectra a major peak at ~398.4 eV, which corresponds to amino nitrogen (-NH₂) of the ligand, suggesting that the amino-functionalized framework is intact after composite synthesis. The deconvoluted peaks in Figure 12d of the O 1s spectra at ~530.6, 528.8, and 532.0 eV are assigned to lattice oxygen (M-O)"Fe-O, Ce-O, ZnO", surface hydroxyl/defect oxygen vacancies, and oxygen atoms in

coordinated carboxylate groups, respectively. Meanwhile, the introduction of CeO₂ and ZnO resulted in the rise in the relative strength of the defect-related oxygen component, which means the production of more oxygen-vacancy-related active sites. The Fe 2p spectra in Figure 12e showed the typical Fe 2p_{3/2} and Fe 2p_{1/2} peaks at around 710.6 and 724.5 eV, respectively, and satellite characteristics, confirming that Fe is mainly in the Fe³⁺ oxidation state in the composite B framework at 716.1 eV. On the one hand, the Ce 3d spectra showed the characteristic multiple splitting of Ce⁴⁺ species, with peaks corresponding to Ce 3d_{5/2} and Ce 3d_{3/2} states. The presence of weak contributions attributed to Ce³⁺ can also be observed of absence of u' peak, which implies the existence of oxygen vacancies in the CeO₂ lattice[37] as illustrated in Figure 12f. The Zn 2p spectra in Figure 12g of ZnO/MIL and CeO₂/ZnO/MIL show two intense peaks at 1021.8 eV (Zn 2p_{3/2}) and 1044.9 eV (Zn 2p_{1/2}) which confirms the existence of Zn²⁺ in the ZnO phase[41]. Composite materials had small binding-energy negligible shifts for Fe 2p, O 1s, Ce 3d and Zn 2p in compared with Literature, which indicates strong electronic interactions between the metal oxides and the MIL framework and the successful construction of CeO₂/ZnO/MIL which leading to enhance the photocatalytic reduction performance of CeO₂/ZnO/MIL composite B. Figure 12h illustrated the U 4f XPS spectrum of Composite B following visible-light photocatalytic experiment. The spectrum can be deconvoluted into two spin-orbit doublets that correspond to U(VI) and U(IV). The dominant peaks at 382.24 eV (U 4f_{7/2}) and 392.72 eV (U 4f_{5/2}) were attributed to U(VI) species, while the additional peaks at 380.38 eV and 391.05 eV are attributed to U(IV). The U(IV) doublet's appearance indicated that a large portion of the adsorbed U(VI) was successfully reduced to U(IV) during visible-light irradiation, rather than being solely adsorbed on the catalyst surface. Meanwhile, the dominant U(VI) peaks indicated that a portion of the uranium remained unreduced or existed as surface-adsorbed U(VI), suggesting that the photocatalytic process involved the coexistence of surface-adsorption and reduction. These results offer direct evidence that the composite B effectively facilitates the transfer of photogenerated electrons for the reduction of U(VI) to U(IV).

To identify the active species involved in the visible-light-driven photocatalytic reduction of U(VI), scavenger experiments were performed using AgNO₃, p-benzoquinone (BQ), isopropanol (IPA), and EDTA-2Na as scavengers for photogenerated electrons (e⁻), superoxide radicals (•O₂⁻), hydroxyl radicals (•OH) and photogenerated holes (h⁺), respectively. The most substantial drop in U(VI) removal (27.0%) compared to the control sample (95.1%) was observed when AgNO₃ was added, which confirmed that photogenerated electrons are the primary reducing species responsible for the conversion of U(VI) to U(IV). The addition of BQ also lowered the reduction efficiency to 68.0%, demonstrating that •O₂ radicals are involved as secondary reactive species in the reduction process. On the other hand, the addition of IPA caused a minor decrease (92%) indicating that the role of •OH radicals are negligible. The removal effectiveness was decreased to 75% with the addition of EDTA-2Na, indicating that holes participate in the reaction pathway, likely through charge separation and interfacial reactions rather than direct reduction of U(VI) as in equations 3-8. Therefore, the contribution of reactive species indicating that the excellent photocatalytic performance of Composite (B) is mainly attributed to the effective electron generation and separation in the heterojunction of CeO₂/ZnO/NH₂-MIL-101(Fe), and superoxide radicals provide an alternative pathway for reduction.



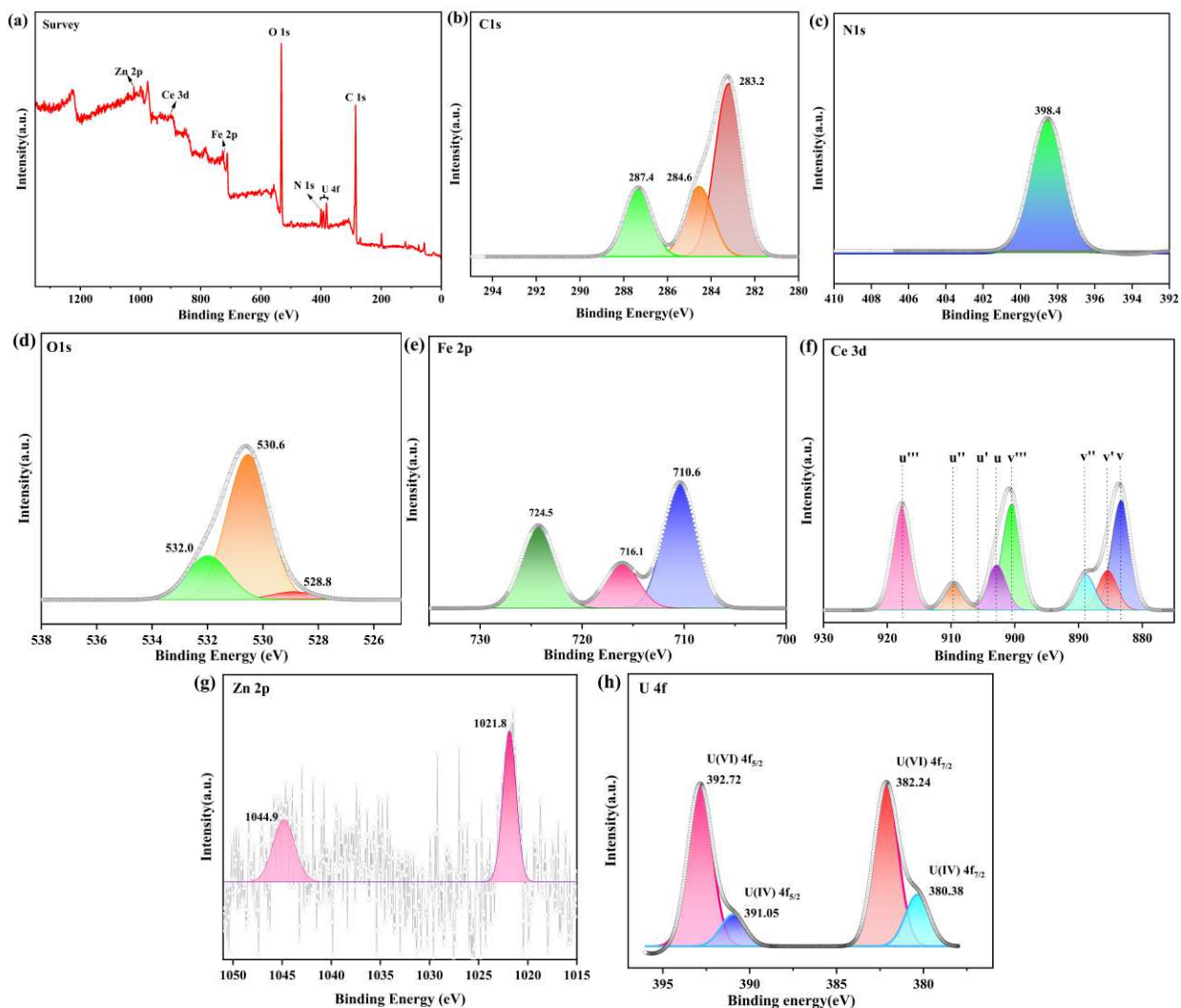
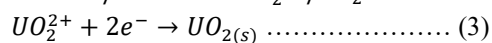
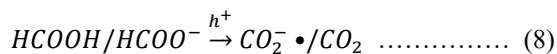


Figure 12. XPS spectra of CeO₂/ZnO/MIL (B): (a) survey; (b) C 1s; (c) N 1s; (d) O 1s; (e) Fe 2p; (f) Ce 3d; (e) Zn 2p; and (h) U Rf.

To further validate the formation of superoxide radicals during the photocatalytic reduction of U(VI), electron paramagnetic resonance (EPR) spin-trapping studies were performed using DMPO under various reaction conditions as in Figure S8. No obvious DMPO-•O₂⁻ signal was found in Composite B or Composite B/HCOOH/U(VI) in the dark, suggesting that superoxide radicals were not formed in the absence of light. Upon visible-light illumination, a typical DMPO-•O₂⁻ signal developed for Composite B, demonstrating that photogenerated electrons converted dissolved O₂ to •O₂⁻ radicals. The signal strength increased substantially with the addition of HCOOH, suggesting that formic acid successfully prevented electron-hole recombination by consuming photogenerated holes, hence increasing the availability of electrons for oxygen activation. The introduction of U(VI) into the Composite B/HCOOH system resulted in a

considerable reduction of the DMPO- $\bullet\text{O}_2$ signal, indicating that a large fraction of the photogenerated electrons was more favorably utilized for the reduction of the adsorbed U(VI) rather than for the generation of superoxide radicals. These EPR results are consistent with the active-species trapping experiments, in which AgNO_3 caused the greatest inhibition of photocatalytic activity, while p-benzoquinone produced a moderate decrease, confirming that photogenerated electrons are the primary active species and $\bullet\text{O}_2$ radicals serve as important secondary reactive species in the U(VI) reduction process.

Conclusion

Herein, $\text{NH}_2\text{-MIL-101(Fe)}$ and a series of CeO_2/ZnO -modified $\text{NH}_2\text{-MIL-101(Fe)}$ composites A, B, and C were successfully synthesized and applied for the visible-light-driven photocatalytic reduction of aqueous U(VI). Structural and physicochemical characterization via PXRD, FT-IR, XPS, UV-vis DRS, and N_2 adsorption-desorption, which confirmed the successful construction of $\text{CeO}_2/\text{ZnO}/\text{MIL}$ heterostructures with the crystalline framework of $\text{NH}_2\text{-MIL-101(Fe)}$. Among the all synthesized photocatalysts, after 60 min of visible-light irradiation, the 5% CeO_2 /10% $\text{ZnO}/\text{NH}_2\text{-MIL-101(Fe)}$ composite was determined to be the most effective photocatalyst for U(VI) reduction with about 92.9% and 95.1% reduction efficiency under air and N_2 atmospheres, respectively. The high efficiency was due to the synergistic interaction between of CeO_2 , ZnO , and $\text{NH}_2\text{-MIL-101(Fe)}$ framework, which facilitated the charge separation, the interfacial electron transfer, and the electron-hole recombination. These results were confirmed by the lowest photoluminescence intensity and shortest charge-transfer resistance of all the tested photocatalysts. Additionally, the reaction conditions have a significant impact on the effectiveness of the photocatalytic reduction. In which, the best results were obtained at pH 5, catalyst dose 75 mg, and initial concentration of U(VI) 20 mg L^{-1} combined with 1% formic acid as sacrificial electron donor. In particular, formic acid was found to greatly improve the photocatalytic reduction as compared to methanol and ethanol, owing to its excellent scavenging of photogenerated holes and improved utilization of electrons. Moreover, radical-scavenging experiments revealed that photogenerated electrons were the dominant active species responsible for U(VI) reduction, while superoxide radicals ($\bullet\text{O}_2^-$) participated as secondary reactive species. Furthermore, the photocatalyst has high stability and recyclability with reduction efficiencies of 78% after five consecutive cycles under N_2 environments, respectively, without loss of structural integrity. All the experimental results confirmed that the rational incorporation of CeO_2 and ZnO into $\text{NH}_2\text{-MIL-101(Fe)}$ is an efficient method for the design of highly efficient visible-light-driven photocatalysts, whereas the optimized $\text{CeO}_2/\text{ZnO}/\text{NH}_2\text{-MIL-101(Fe)}$ composite has a great potential for reduction and immobilization of soluble radionuclide species in aqueous environments and provides a viable strategy for the treatment of radioactive wastewater with U(VI) pollutant.

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Declarations

Competing interests The authors declare no competing interests.

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