Design and preparation of Ag/AgCl/NH₂-MIL-101 (Fe) ternary composite photocatalysts with visible light application prospects

Chunhua Xu¹*

¹ Dalian Vocational & Technical College (Dalian Radio and TV University), Dalian, Liaoning, 116035, China
Husong@hust.edu.cn
*Corresponding author’s e-mail: xuchunhua0331@163.com

Abstract. In this work, Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalysts were designed and constructed by an in-situ UV reduction method. Simultaneously, the characterization of the sample mainly included X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The sample displayed excellent performance and stability of water, air and ultraviolet light in the preparation process. The formation mechanism was proposed based on the cooperation of the reaction between Ag⁺ and Cl⁻ in NH₂-MIL-101 (Fe) and ultraviolet reduction. The Electron Spin Resonance (ESR) results demonstrated that the main active oxygen species were •OH and •O₂⁻ in the photocatalytic process. This work would provide a novel strategy for synthesizing highly efficient photocatalysts in the visible light field.

1. Introduction
Green and efficient photocatalysis technology is favored by more and more researchers[1]. Metal-organic frameworks (MOFs) are a promising catalyst, which has a wide range of applications in many fields such as organic matter conversion and pollutant treatment. The photocatalytic responsiveness of MOFs can be attributed to the generation of photogenerated electrons-holes (e⁻-h⁺) pairs: under light conditions, when the incident light energy is greater than the bandgap energy (Eg) of the semiconductor catalytic material, the electrons located in the valence band (VB) absorb energy and transition to conduction band (CB), while leaving holes in the VB, thereby generating temporarily separated e⁻-h⁺ pairs. The electrons located in the VB and the CB can respectively undergo redox reactions on the substrate or generate reactive •OH and •O₂⁻[2]. Although the time being studied of MOFs in the field of photocatalysis is very short, Fe-MOFs still show good application prospects in the field of visible light catalysis. It’s because that Fe is the second most abundant metal element on earth and iron-oxo (Fe-O) cluster of Fe-MOFs shows good absorption response performance in the visible light range[3]. Xie et al. successfully constructed NH₂-MIL-88B (Fe) to highly sensitive detection and effective degradation of heavy metal ions in water[4]. However, the traditional Fe-MOFs have some shortcomings that limit its application in visible light catalysis. For example, even if Fe-MOFs is irradiated by incident light, the excited photo-generated electrons easily release energy and return to the valence band to recombine with holes, thereby losing photocatalytic activity. In view of the shortcomings of Fe-MOFs, researchers found that loading precious metals on the original catalyst is an effective method. Silver has surface plasmon resonance (SPR) effect, and it can
effectively expand the absorption intensity of the catalyst in the visible light region when loaded on MOFs[5]. Moreover, when silver nanoparticles are loaded on the MOFs, a heterostructure can be formed, which facilitates the transfer of photogenerated carriers, thereby effectively making up for the shortcomings of the high photogenerated e⁻h⁺ recombination rate of Fe-MOFs alone[6]. Based on this, we designed the Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalyst. Through characterization and testing of free radical active species, it has proved its promising application prospects for photocatalysis.

2. Experimental sections
The spindle-shaped NH₂-MIL-101 (Fe) was synthesized through a solvothermal method. Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalyst was prepared via an ultraviolet light reduction method. In brief, ethanol, silver nitrate and NH₂-MIL-101 (Fe) were added to the beaker under ultrasonic and magnetic stirring at room temperature, forming a uniform suspension. The suspension was transferred to a dark box, accompanied by magnetic stirring, a high-pressure mercury lamp (light intensity about 100 mW cm⁻²) was used for in-situ ultraviolet light reduction reaction, and then a series of post-treatments were carried out to obtain the final product.

3. Results and discussions
3.1 Structure and composition analysis
The crystalline structure of the composite photocatalyst Ag/AgCl/NH₂-MIL-101 (Fe) was characterized as displayed in Figure 1. Compared with the XRD spectrum of NH₂-MIL-101 (Fe), it showed that the crystalline structure of NH₂-MIL-101 (Fe) was unchanged during the process of reducing the loaded Ag/AgCl by ultraviolet light, which indicated that NH₂-MIL-101 (Fe) had excellent stability of water, air and ultraviolet light. In contrast to the standard cards, it demonstrated that the diffraction peaks appeared at 27.8°, 32.2°, 46.2°, 54.8° and 57.5° in the XRD spectrum of Ag/AgCl/NH₂-MIL-101 (Fe), which were attributed to the crystal planes of cubic phase AgCl at (111), (200), (220), (311) and (222), and the lattice parameter was a=4.0862 Å (JCPDS File No.31-1238)[7]. Simultaneously, the diffraction peaks appeared at 38.1° and 44.3° were attributed to the crystal planes of cubic phase Ag at (111) and (200), and the lattice parameter was a=5.5491Å (JCPDS File No. 04-0783)[8]. Additionally, the diffraction peaks of NH₂-MIL-101 (Fe) were unchanged or unshift significantly, and no other diffraction peaks were found in the XRD spectrum of the Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalyst, which further indicated that Ag/AgCl nanoparticles were not doped into the lattice of NH₂-MIL-101 (Fe), but were only supported on the surface of NH₂-MIL-101 (Fe). The characteristic diffraction peak intensity of Ag was weaker, which might be related to the smaller amount of Ag formed. It could be preliminarily judged by XRD characterization that the Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalyst was successfully prepared by the in-situ photoreduction method, and the NH₂-MIL-101(Fe) displayed excellent performance and stability of water, air and ultraviolet light in the preparation process.
Figure 1 X-ray diffraction patterns of Ag/AgCl/NH2-MIL-101 (Fe) samples

The morphology of the Ag/AgCl/NH2-MIL-101 (Fe) in the SEM and TEM images was shown in figure 2a-c. As displayed in figure 2a, the Ag/AgCl nanoparticles were relatively uniformly distributed on the surface of the spindle-shaped NH2-MIL-101 (Fe). The diameter of the Ag/AgCl nanoparticles was in the range of 10-40 nm, and deposited on the surface of spindle-shaped NH2-MIL-101 (Fe) with a length of about 0.5-1.2 µm and a width of about 300 nm. It could be further observed from the TEM image that some small Ag/AgCl nanoparticles were loaded on the spindle-shaped NH2-MIL-101 (Fe), as shown in figure 2b. Figure 2c was the HRTEM image of Ag/AgCl/NH2-MIL-101 (Fe) composite photocatalyst. The lattice spacing d=0.236 nm corresponded to the (111) crystal plane of cubic phase Ag, and the lattice spacing d=0.277 nm corresponded to the (200) crystal plane of cubic AgCl, which were consistent with the analysis results of XRD spectrum. The characterization of SEM and TEM further proved that Ag/AgCl composite nanoparticles were loaded on the surface of NH2-MIL-101 (Fe).

3.2. XPS analysis

The XPS spectrum of the prepared Ag/AgCl/NH2-MIL-101 (Fe) composite photocatalysts were displayed in figure 3a. The sample mainly contains C, N, O, Cl and Ag elements, which was consistent with the composition of Ag/AgCl/NH2-MIL-101 (Fe) composite photocatalyst. Figure 3b displayed that the characteristic single peak at 532.1 eV was the O 1s peak, which was confirmed to Fe-O. The XPS spectrum of Cl 2p was displayed in figure 3c, which the binding energies of Cl 2p1/2 and Cl 2p3/2 were 197.98 eV and 199.38 eV respectively, and the peak spacing was 1.4 eV. Compared with the standard spectrum, it could be judged that the chlorine in the prepared Ag/AgCl/NH2-MIL-101 (Fe) composite photocatalyst was Cl[9]. In figure 3d, characteristic peaks at 284.6 eV, 285.7 eV and 288.7 eV corresponded to the C-C, C-O and C=O of organic ligand, respectively[10]. As shown in figure 3e, the Ag 3d peaks at 367.5 eV and 373.5 eV were attributed to the Ag 3d3/2 and Ag 3d5/2 peaks of Ag (I) in AgCl respectively, and the peak spacing was 6.0 eV. In addition, the peaks at 368.1 eV and 374.1 eV could be verified to the Ag 3d3/2 and Ag 3d5/2 peaks of

Figure 2 SEM (a) and TEM (b-c) of the Ag/AgCl/NH2-MIL-101 (Fe) samples
the simple substance of Ag, and the peak spacing was 6.0 eV[11-13], which indicated that Ag/AgCl/NH2-MIL-101(Fe) contained two forms of Ag, namely Ag(I) and Ag(0), thereby it was consistent with the XRD and HRTEM characterization results. In figure 3f, Fe 2p had three sets of peaks, of which 712.6 eV and 726.3 eV corresponded to Fe 2p3/2 and Fe 2p1/2 respectively, which indicated that Fe in the spindle morphology NH2-MIL-101 (Fe) and the satellite peak with a binding energy of 717.8 eV was also classified as Fe(III)[14]. Combined with the analysis results of XRD, TEM and XPS, it could be further determined that the prepared Ag/AgCl/NH2-MIL-101 (Fe) composite photocatalyst was composed of three components.

3.3. Formation mechanism analysis
Charaterization by XRD, SEM, TEM and XPS could confirm that the Ag/AgCl/NH2-MIL-101 (Fe) composite photocatalyst had been successfully prepared. Furthermore, it was speculated that the formation mechanism of its structure was shown in figure 4. In the preparation process of NH2-MIL-101 (Fe), FeCl3·6H2O was used as the Fe precursor of NH2-MIL-101 (Fe) and Cl ions participated in the formation of crystals. The chemical composition of the spindle morphology NH2-MIL-101 (Fe) was Fe3O(H2O)2Cl[C6H4(CO2)2NH2]3[15]. Cl ions could coordinate with the unsaturated Fe3+ in NH2-MIL-101 (Fe), so as to be uniform and stable in the prepared NH2-MIL-101 (Fe) crystal structure. When NH2-MIL-101 (Fe) was added to AgNO3 solution, the solubility product (Ksp) of AgCl was small (about 1.8×10^-10 mol^2•L^-2), thereby Cl ion would dissociate from the NH2-MIL-101 (Fe) crystal structure, and preferentially formed AgCl nanoparticle precipitation with Ag+, which would deposit to the surface or pores of the spindle morphology NH2-MIL-101 (Fe). Thence, under the reduction effect of ultraviolet light, a part of the Ag+ in the AgCl nanoparticles was reduced to form the elemental metal Ag, thereby forming Ag/AgCl composite nanoparticles. Moreover, a certain amount of Ag/AgCl nanoparticles were formed on the surface and pores of the spindle morphology NH2-MIL-101 (Fe), the further formation of Ag/AgCl nanoparticles in the solution could be inhibited.
3.4. ESR analysis

Figure 5a-b displayed the ESR spectrum of the spin-trapping DMPO-•OH and DMPO-•O₂⁻ adduct generated by the Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalyst dispersed in water and methanol respectively under visible light conditions. There was no characteristic signal peak of the DMPO-•OH adduct in the dark state, by contrast, there were obvious quartet characteristic peaks under visible light irradiation in the ESR spectrum, and the peak intensity ratio was 1:2:2:1 approximately, which was an obvious characteristic signal peak of DMPO-•OH adduct[16]. Similarly, there was no characteristic signal peak of the DMPO-•O₂⁻ adduct in the dark state, by contrast, there were obvious quartet characteristic peaks under visible light irradiation in the ESR spectrum. This result confirmed that the Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalyst system was irradiated with visible light, electron-hole separation occurred on the surface. The photogenerated holes reacted with the adsorbed H₂O on the surface to form •OH reactive oxygen species (ROS), and the photogenerated electrons reacted with the adsorbed O₂ around to form •O₂⁻ ROS. The ESR research consequences demonstrated that Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalyst might have a better application prospect in the visible light field.

Figure 5 ESR spectra in Ag/AgCl/NH₂-MIL-101 (Fe) suspension solution after 60 seconds under visible light irradiation (λ > 400 nm): (a) DMPO-•OH formed in irradiated aqueous suspension; (b) DMPO-•O₂⁻ formed in irradiated methanol suspension

4. Conclusions

In conclusion, a novel Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalysts were successfully designed and prepared by an ultraviolet light reduction method. The particle size range of Ag/AgCl composite nanoparticles was 10-40 nm, and their formation originated from the reaction of Cl⁻ in NH₂-MIL-101 (Fe) with Ag⁺ and the reduction effect of ultraviolet light. The morphology and structure of Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalysts were characterized by XRD, SEM, TEM and XPS, and the formation mechanism of composite photocatalysts were proposed. The ROS
generated in the reaction process was studied through ESR technology, and on this basis, Ag/AgCl/NH₂-MIL-101 (Fe) composite photocatalyst might have a better application prospect in the visible light field.

Acknowledgments
Thanks to the 2020 School-level Scientific Research Project of Dalian Vocational & Technical College (Dalian Radio and TV University).

References
[1] Zhang, T., Lin, W. (2014) Metal-organic frameworks for artificial photosynthesis and photocatalysis. Chem Soc Rev, 43: 5982-5993.
[2] Zhu, B., Zou, R., Xu, Q. (2018) Metal-Organic Framework Based Catalysts for Hydrogen Evolution. Advanced Energy Materials, 8: 1801193.
[3] Liang, R., Jing, F., Shen, L., Qin, N., Wu, L. (2015) MIL-53(Fe) as a highly efficient bifunctional photocatalyst for the simultaneous reduction of Cr(VI) and oxidation of dyes. J Hazard Mater, 287: 364-372.
[4] Xie, D., Ma, Y., Gu, Y., Zhou, H., Zhang, H., Wang, G., Zhang, Y., Zhao, H. (2017) Bifunctional NH₂-MIL-88(Fe) metal–organic framework nanoctahedra for highly sensitive detection and efficient removal of arsenate in aqueous media. Journal of Materials Chemistry A, 5: 23794-23804.
[5] Zhang, Z., Wang, S., Bao, M., Ren, J., Pei, S., Yu, S., Ke, J. (2019) Construction of ternary Ag/AgCl/NH₂-Uio-66 hybridized heterojunction for effective photocatalytic hexavalent chromium reduction. J Colloid Interface Sci, 555: 342-351.
[6] Xu, H., Xie, J., Jia, W., Wu, G., Cao, Y. (2018) The formation of visible light-driven Ag/Ag₃O photocatalyst with excellent property of photocatalytic activity and photocorrosion inhibition. J Colloid Interface Sci, 516: 511-521.
[7] Shang, M., Wang, W., Lu, C., Ren, J., Zhou, L., Zhang, L. (2009) Efficient visible light-induced photocatalytic degradation of contaminant by spindel-like PANI/BiVO₄. J Phys Chem C, 113: 20228-20233.
[8] Wang, P., Huang, B., Qin, X., Zhang, X., Dai, Y., Wei, J., Whangbo, M.H. (2008) Ag@AgCl: a highly efficient and stable photocatalyst active under visible light. Angew Chem Int Ed Engl, 47: 7931-7933.
[9] Bi, Y., Ye, J. (2009) In situ oxidation synthesis of Ag/AgCl core-shell nanowires and their photocatalytic properties. Chem Commun (Camb), 6551-6553.
[10] Wu, Y., Luo, H., Wang, H. (2014) Synthesis of iron(iii)-based metal–organic framework/graphene oxide composites with increased photocatalytic performance for dye degradation. RSC Adv., 4: 40435-40438.
[11] Wang, P., Huang, B., Lou, Z., Zhang, X., Qin, X., Dai, Y., Zheng, Z., Wang, X. (2010) Synthesis of highly efficient Ag@AgCl plasmonic photocatalysts with various structures. Chemistry, 16: 538-544.
[12] Tang, Y., Jiang, Z., Xing, G., Li, A., D.Kanhere, P., Zhang, Y.Y., Sum, C.T., Li, S.Z., Chen, X.D., Dong, Z.L., Chen, Z. (2013) Efficient Ag@AgCl cubic cage photocatalysts profit from ultrafast plasmon-induced electron transfer processes. Adv Funct Mater, 23: 2932-2940.
[13] Ma, B., Guo, J., Dai, W.-L., Fan, K. (2012) Ag-AgCl/WO₃ hollow sphere with flower-like structure and superior visible photocatalytic activity. Applied Catalysis B: Environmental, 123-124: 193-199.
[14] Guo, S., Li, X., Wang, H., Dong, F., Wu, Z. (2012) Fe-ions modified mesoporous Bi₂WO₆ nanosheets with high visible light photocatalytic activity. J Colloid Interface Sci, 369: 373-380.
[15] Laurier, K.G.M., Vermoortele, F., Ameloot, R., De Vos, D.E., Hofkens, J., Roelfsaeers, M.B.J. (2013) Iron(III)-Based Metal–Organic Frameworks As Visible Light Photocatalysts. Journal
of the American Chemical Society, 135: 14488-14491.

[16] Chen, D., Yoo, S.H., Huang, Q., Ali, G., Cho, S.O. (2012) Sonochemical synthesis of Ag/AgCl nanocubes and their efficient visible-light-driven photocatalytic performance. Chemistry, 18: 5192-5200.