Research progress of Cu/Fe-MOF composites applied in water treatment process

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Abstract. With a rapid growth of industry and agriculture, the problem of increasing levels of industrial by-products, organic dyes, drugs and personal care products, pesticides, and insecticides contaminants in the water environment needs to be addressed urgently. Cu-based organic framework material (Cu-MOF) is non-toxic, stable, easy to introduce functional groups and easy to assemble. Fe-based organic framework material (Fe-MOF) is strong in reactivity, fast in electron transfer capability, mostly magnetic and easy to recover, thus the combination of the two composite materials can take advantages of the both. The high efficiency water treatment material with green environmental protection and no secondary pollution was prepared, which had broad application prospect in the field of water treatment. In this paper, the construction and application process of Cu-MOF, Fe-MOF, Cu/Fe-MOF and Cu/Fe-MOF derivatives were reviewed, and the further development of these materials in the field of water treatment was prospected.

1. Introduction

With the rapid development of industry and the growth of population, the problem of water safety has attracted more and more attention. Metallic organic frame (MOF) has the advantages of ultra-high porosity, large specific surface area, adjustable function and structure, high thermal stability and strong chemical durability. In recent years, it has been fully applied to treat pollutants such as industrial by-products, organic dyes, drugs and personal care products, pesticides and insecticides in water bodies.

Fe-MOF and Cu-MOF refer to the use of different organic ligands to coordinate and polymerize Fe or Cu to form metal organic framework material. Due to its numerous surface functional group and large specific surface area, it has strong adsorption [1] or catalytic degradation ability of pollutant [2]. This paper reviews the research progress in the preparation and environmental application of Cu-MOF, Fe-MOF, Cu/Fe-MOF symbiosis and Cu/Fe-MOF derivatives.

2. Construction of Cu/Fe-MOF composites

Many scholars have studied how to improve the pollutant removal performance of Fe-MOF and Cu-MOF composites. The improvement of pollutant removal performance of Cu-MOF materials is mainly achieved by improving surface structure, introducing non-steady state ligand and other chemical means [3, 4].

In order to solve the problem of catalyst expansion caused by electron transfer, LU [5] et al. took nickel foam as the skeleton. Polyaniline (PANI) is used to induce MOF-74 precursor (metal =Co, Fe, organic ligand =2, 5-dihydroxyterephthalic acid (H_2DODC, $C_8H_6O_6$)) to change crystal growth and orientation. Nanorod array (NRAs) structures MOF-74-Co/Fe-NRAs (FIG. 1) are then grown on the surface of nickel foam. The ordered structure of the material can evenly distribute Fe metal elements in the gap between O and Co, providing a good bridging effect for the electron transfer of O between different valence metals.

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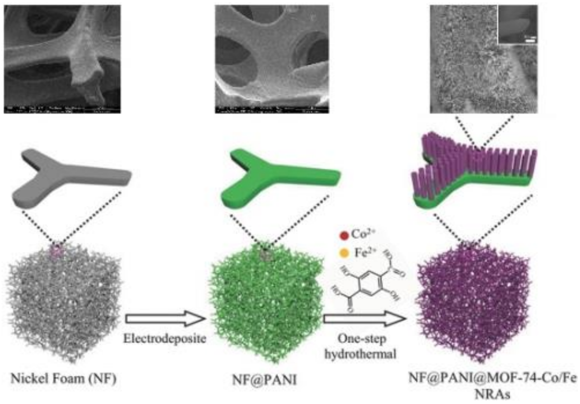

Figure 1. Synthesis process of NF@PANI@MOF-74-Co/Fe-NRAs and SEM images of each component

CHENG [3] used Cu_2O nanoscale box (NBs) as matrix and 2, 3, 6, 7, 10, 11-hexahydroxytriphenyl as organic ligand (FIG. 2). A conductive honeycomb Cu-MOF layer was prepared on the surface of Cu_2O nanoscale box by solution thermal method. Cu-MOF layer with thickness of 20 nm enhances the stability of nanostructure and accelerates the reaction of water to resolve hydrogen.

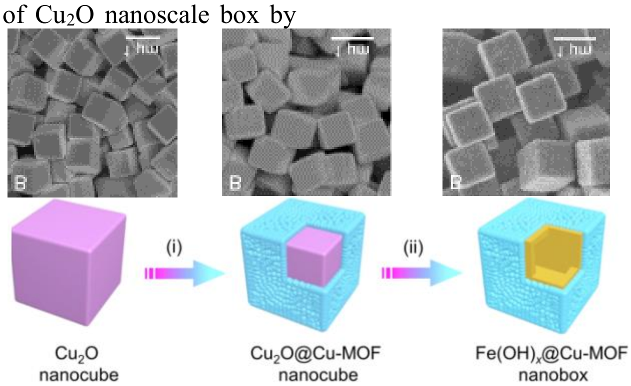

Figure 2. Synthesis process of [Fe(OH)]x@Cu-MOF NBs and SEM images ofdifferent stages

Fe-MOF or Cu-MOF materials alone are small in size, easy to disperse, difficult to collect, and easy to cause secondary pollution. Therefore, the formation of Cu / Fe-MOF composites can effectively adjust MOF structure by greatly changing the functional structure of material surface. The bimetallic organic framework theory can effectively remedy the obvious defects of a single material. The catalytic degradation and adsorption performance of pollutants are effectively improved.

3. Application of Fe/Cu-MOF composites in water treatment process

3.1 Fe-based material loading Cu-MOF

Fe-based materials are loaded with Cu-MOF in a variety of ways, such as assembling Fe-based granular materials on the surface of Cu-MOF, Fe-based granular materials embedded in Cu-MOF [6] and Cu-MOF coating Fe-based materials Pu [7], etc. A large number of intermediate by-products such as nitrile, isocyanate, isothiocyanate and isocyanide are easily produced in the industrial production process, which has the characteristics of high concentration, complex structure and difficult degradation. Cu/Fe-MOF composites can selectively catalyze the removal of such pollutants by corresponding functional group.

ARASH [8] developed magnetic metal-organic framework Fe_3O_4@GlcA@Cu-MOF material in high temperature solution. Nitrile, isocyanate, isothiocyanate and isocyanide were removed during the synthesis of thioamide. Selective transfer hydrogenation occurred on the surface of the composite material. The material exhibits good electrochemical properties and reduces the presence of nitriles, isocyanates, isothiocyanates and isocyanides. The material has good thermal stability. Moreover, the leaching rate of heavy metals after the catalytic process is extremely low, which greatly avoids the generation of toxic by-products during the degradation process. However, there are some problems such as strict reaction conditions, difficult recovery of catalyst and complicated procedure.

Loaded MOF can also be applied to the treatment of pharmaceutical wastewater. Based on a large number of researches on antibacterial behavior, AZIZABADI [7] developed a stable metal-organic framework that enhances sterilization performance and continuously affects bacteria by systematically considering biocompatibility, biodegradability, economic feasibility and other factors. Nanoscale core-shell Fe_3O_4@Cu-MOF structures were synthesized by ultrasound-assisted reverse micellar method with Fe_3O_4 and Cu-MOF (metal =Cu, organic ligand =2, 6-pyridinic acid). First of all, nanoscale Fe_3O_4 improves the physical and chemical properties of the Cu-MOF structure. While enhancing the specific surface area, it significantly improves the material stability and avoids the problem of Cu-MOF hardening due to polymerization tendency and the problem that Cu ions cannot be released permanently. Secondly, the positively charged Fe in Fe_3O_4 attracts negatively charged bacteria through electrostatic action, which damages the bacteria and makes the organism lose its activity. Finally, nanometer Fe_3O_4 particles also enhance the magnetic and repurpose properties of the material. In the experiments of Staphylococcus aureus and Escherichia coli, Cu-MOF was selected as the shell structure as Fe_3O_4 storage unit because of its low toxicity to humans and high toxicity to bacteria. Synthesis process is shown in Figure 3.

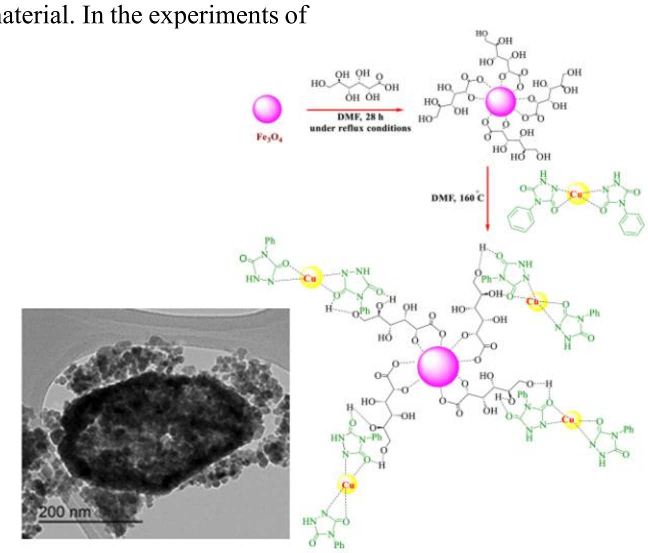

Figure 3. Synthesis process of Fe_3O_4@Cu-MOF nano-particles

3.2 Cu-based material loading Fe-MOF

Cu-based material loading Fe-MOF method is similar to Fe-based material loading Cu-MOF method. For example, Cu-based granular material is assembled on the surface of Fe-MOF [9], and Cu-based granular material is bridged into the Cu-MOF [10].

HE [9] used steam reduction method to construct sites that could support Cu stably with MIL-100 (metal =Fe, organic ligand =H_3BTC) as matrix. Through the methanol steam reduction at 200 ℃, supported by iron-based skeleton, the conversion of Cu^{2+} to Cu elemental substance is realized 100%, and part of Fe^{3+} is converted to Fe^{2+} at the same time.

ZHONG [10] successfully constructed Cu_2O / MIL on the surface of MIL-100 (Fe / Cu) (metal = Fe, Cu, organic ligand = H_3BTC) organic framework by a step-by-step thermal solution synthesis method. During synthesis process, original MIL-100 material has an irregular octahedral structure. After Cu is introduced into MIL-100 material, it competes with Fe^{3+}, which promotes the growth of crystal and produces new crystal phase. As a result, particle size increases, crystal integrity decreases and the surface becomes rough. Experiments show that the single Cu_2O and MIL-100 materials do not have the ability to separate hole electron pairs. In the composite material, Cu_2O can effectively absorb visible light and generate photogeneration current. Furthermore, more reactive oxygen species (·O_2- and ·OH) are generated, which significantly improved the catalytic degradation performance of thiacloprid.

3.3 Cu / Fe-MOF symbiotic growth

In addition to prepare Cu and Fe-based materials and loading them with another MOF material, many scholars have prepared bimetallic MOF materials by introducing Fe and Cu bimetallic nodes into the synthetic MOF at the same time.

TANG [11] prepared Fe / Cu-BDC (metal = Cu, Fe, organic ligand = terephthalic acid (H_2BDC, $C_8H_6O_4$)) based on simple hot solution method. The composite material can completely remove sulfamethoxazole (SMX $C_{10}H_{11}N_3O_3S$), which provides a new idea for the treatment of wastewater containing pharmaceutical pollutants. SIEW [12] constructed Fe/Cu-BTC bimetallic organic framework materials by mixing Cu-BTC and Fe-BTC synthesized separately with water as medium. By modifying the surface morphology and pore size, it shows good adsorption performance for methyl blue.

3.4 Cu / Fe-MOF derivative

Cu / Fe-MOF derivatives are mostly based on MOF materials as templates. Through pyrolysis under inert gas, porous carbon materials, metal and metal oxide materials, MOF polymer composite materials and other derivatives with carbon matrix as the matrix are produced. The original MOF skeleton can be maintained while avoiding the accumulation of metal elements. It exhibits superior thermal stability and excellent performance in catalysis and adsorption.

TANG [11] first prepared Cu / Fe-MOF by one-pot synthesis method, and then pyrolyzed the bimetallic MOF precursor in a tube furnace to synthesize 3D nano-flower FeCu@C by sacrificial template method. It was found that nearly 50% of the degradation was caused by the removal of active substances generated by the activation of defect sites on the surface of materials. Cu / Fe-MOF heterogeneous catalytic degradation is adopted, which is environmentally friendly while removing pollutants.

AYDAN [13] used a sacrificial template method to prepare FeOOH@$Cu_3(BTC)_2$ by ultrasonic one-pot synthesis and then pyrolyzed the material to

Fe_3O_4@Cu_xO_y/C for the degradation of the organic pollutant 4-nitrophenol.

4. Conclusion

As a kind of popular high-performance materials, MOF has received extensive attention in the field of water treatment due to its extremely high specific surface area and flexible assembly structure.

- When Cu-MOF is used as the matrix, the main purpose of introducing Fe element is to change the crystal structure, reduce the crystallinity of the crystal, promote the transformation of pores from capillaries to mesoporous or mesoporous, and promote the pollutant to fully contact the reaction activity check point inside the material. Secondly, the formation of Cu coordination unsaturated, which in turn shows excellent catalytic or adsorption properties.
- When Cu element is introduced into Fe-MOF matrix, the crystal is expected to grow again. Through the competitive coordination between Fe and Cu, unique Cu-Fe clusters are formed under different reaction conditions. To improve the surface properties of the material, such as oxygen vacancy and other structural defect sites. Thus, it has excellent pollutant removal performance
- Synthetic materials with Cu / Fe coexistence show the same characteristics of the two. The material is fully dispersed locally. More metal activity check points are exposed to the mass transfer range of pollutants.

Therefore, bimetallic organic framework materials complement each other and combine the advantages of the two. It shows a bright application prospect in the field of water treatment.

Acknowledgments

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