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A Review of Applications of Zn-Mofs in Nuclear Industry and Biology

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Abstract: *Metal-organic Frameworks (MOFs) are a type of rapidly developing crystalline material which contain potential interstitial light-emitting metal-organic frameworks (LMOFs) with a wide range of potential applications. In this paper, the microstructure and preparation methods of common Zn-MOFs are mainly introduced. And for its special properties are classified and summarized, plus the current application scenarios. Based on this, the latest progress in this field is reviewed, and the future research in this field is prospected.*

Keywords: *Zn-MOFs Metal-Organic Frameworks; fluorescence*

1. Development status of MOFs

With the arrival of the era of science and technology, all walks of life have ushered in a period of rapid development. The following pollution problems are becoming more and more serious. Radioactive particle pollution is difficult to control. Therefore, the detection of radioactive ions has become more and more urgent [1]. There are obvious adverse effects on human health when exposed to radioactive elements. The kidney is the main organ exposed to radioactive elements through food and non-food, so it will cause irreversible damage to the kidney [2]. In addition, with the extensive use of nuclear energy in countries with nuclear technology in the world, the demand and use of uranium materials have increased accordingly [3]. Scientific research shows that uranium exists in an aqueous solution in the form of uranyl ion (UO_2^{2+}). The Fukushima nuclear accident resulted in nuclear leakage in 2011, which posed a great threat to people's safety. Due to the chemical and radiation toxicity of uranium, when normal people are exposed to uranium, direct exposure to uranium will increase the risk of cancer or liver and kidney damage [4]. Therefore, the detection of these heavy metal ions with high selectivity and sensitivity is of great significance to environmental safety and human health. Cadmium is a naturally occurring heavy metal that is radioactive and often found in heavy industry sites and nuclear waste water. According to the World Health Organization (WHO), cadmium ion in drinking water should not be higher than about 40 nM, otherwise it will cause irreversible damage to the human body [5]. Therefore, it is necessary to establish a sensitive detection method for cadmium ion. In addition, many industries produce radioactive gases used to recover important minerals from various bioenergy stores [6].

Up to now, many analytical techniques have been used for various ion detection, such as X-ray fluorescence spectroscopy (XRF), atomic fluorescence spectroscopy (AFS), atomic absorption spectroscopy (AAS) and so on. However, they all have some problems including high cost, long test time, and no real-time monitoring. Therefore, it is urgent to develop new methods for detecting radioactive metal ions. At present, fluorescence sensors with simple use, low cost and portability have been recognized by scientists and widely used [7]. Metal-organic frameworks (MOFs) are the most promising fluorescent sensor materials. They have attracted much attention because of their large specific surface area, adjustable aperture, and strong functionalization ability [8]. In recent years, many luminescent MOFs have been successfully synthesized and used in various ions and molecules sensor [9]. It is found that MOFs based on transition metal ions (Zn^{2+} ions) has strong sensitivity as a dual-function sensor to detect toxic metal ions Pb^{2+} and radioactive ions UO_2^{2+}. Compared with lanthanide MOFs, transition metals, especially Zn-MOFs, are more economical, have a wide range of raw materials, and are stable in water. Therefore, the research on Zn-MOFs is advancing rapidly all over the world, hoping to effectively replace the current detection methods.

2. Microstructure of Zn-MOFs

At present, most of the known sensing materials are based on fluorescence quenching reactions.

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However, metal skeletons are rarely used to detect the opening behavior of radioactive and toxic elements, although sensing devices are more sensitive to them [10]. Therefore, in order to realize the specific application of zinc-based MOFs in practice, the structural design of MOFs is the most important part. So far, numerous Zn-MOFs structures have been interviewed, and the most common structures are described below.

2.1. 3D Pillared-Layered Zn-MOFs

Three-dimensional pillared layered Zn-MOFs are a type of MOFs constructed from extended π conjugated aromatic organic ligands. It can be used as an antenna to increase the energy loss, luminescence, and conversion intensity of MOFs [11]. In addition, the long extension joints of organic groups can be used as the pillars of the MOFs structure to stabilize the structure. It should not be ignored that the soft donor site is an important aspect of weight matching, which determines part of the performance of MOFs. Because most of the radioactive heavy metals such as Cd^{2+}, Hg^{2+}, Pb^{2+} and so on are asthenic acid or intermediate acid. According to the above, the soft donor site reacts with radioactive heavy metals according to the HSAB principle. On this basis, a new Zn-MOFs was constructed by using zinc nitrate and flexible ligand. In this novel MOFs, the sulfur element does not bind to any metal center, creating favorable chemical conditions for the sensing sensitivity and small molecule capture of MOFs. Because of this, 3D Pillared-Layered Zn-MOFs can selectively detect Cd^{2+}, a radioactive metal ion, and pick up iodine molecules.

2.2. Carboxyl-functionalized Zn (II)-MOF

Carboxyl-functionalized Zn (II)-MOFs is a metal skeleton of carboxyl functional groups prepared under hydrothermal conditions. At present, most MOFs use bipy and H3L as ligands. First, bipy has the ability to effectively stabilize the coordination network and stabilize the overall architecture because it acts as a bridging ligand. H3L has a π conjugated structure, which is a good electron donor and can contribute electrons. The formation of MOF also partly comes from the coordination of carboxyl oxygen atom transition metal ions and carboxyl oxygen atom. At this point, uncoordinated carboxyl groups and excess carboxyl groups can be used as preparatory functional groups [12]. Finally, carboxyl-functionalized Zn (II)-MOFs is a three-dimensional skeleton structure with multiple single-peak interconnections, in which some carboxyl groups are not coordinated. Therefore, they have high accuracy, high sensitivity and high selectivity, and can be used as fluorescent probes for the detection of heavy metal radioactive ions Pb^{2+} and UO_2^{2+}, and can be applied in complex aqueous environment.

2.3. Multi-responsive Zn-MOFs

For multi-responsive Zn-MOFs, the ligand is usually benzene tetracarboxylic acid. H4bta has a carboxyl group and eight potential donor atoms in its structure, so it can realize the existing size structure and topological structure, and can be achieved from multiple angles and dimensions. In addition, it contains four carboxyl groups, allowing partial or complete deprotonation of the entire structure. Moreover, it contains a large number of hydrogen bonds, which can effectively provide donor and receptor, making it an ideal ligand for constructing supramolecular networks and controlling the degree of deprotonation. Therefore, it may be ideal for building multidimensional MOFs. Many MOFs, though, contain H4bta ligands to stabilize three-dimensional structures. However, using MOFs based on H4bta ligands as fluorescence sensors still presents many problems and challenges for scientists [13]. Therefore, it is necessary to study fluorescence sensing and coordination chemistry for multi-responsive Zn-MOFs.

3. Properties of Zn-MOFs

3.1. Adsorption of Radioactive Ions

Uranium is the basic material of fuel pellets in nuclear industry. Driven by the energy crisis, the wide use of uranium also brings about various environmental problems. Currently, scientists have a simple and easy way to achieve uranium adsorption via a post-coordination modification synthesis strategy. They grafted coumarin to the coordination unsaturated Zn (II) center and prepared a series of coumarin-modified Zn-MOFs-74. The experimental results show that the sample has ultra-high adsorption capacity for U(VI) ions in water at pH 4, and the maximum adsorption capacity can reach 360 mg g^{-1} [14]. And in addition, produced self-driven micromotors based on MOFs and demonstrated the potential for

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efficient removal of radioactive uranium by Fe doping into the ZIF-8 to ensure structural stability and efficient removal of radioactive uranium (96%) from aqueous solution within one hour in the presence of fuel (hydrogen peroxide) and acidic media. The recovery is then carried out under magnetic control, which has stable recycling capacity and high selectivity [15].

3.2. Fluorescent Sensors

Functionalized metal-organic framework materials themselves have different luminescence mechanisms. There are four main types of luminescence: fluorescence based on organic ligands, metal-center emission fluorescence (the so-called antenna effect), charge transfer such as ligand-to-metal charge transfer (LMCT) and metal-ligand-to-metal charge transfer (MLCT) guest molecules and MOFs [16]. Organic ligand luminescence refers to a series of changes, including internal conversion or vibration relaxation, intersystem hopping, fluorescence and phosphorescence, when organic ligand molecules absorb a certain amount of photon energy. The 4f electron layer represented by the lanthanide metal is unfilled state. These unfilled 4f electron structures lead to complex multistate energy levels. The lanthanide ion light absorption and light emission mainly come from the transition between these 4f electrons. Charge transfer luminescence refers to the process of charge transfer from excited state to ground state. Generally, there are ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) in MOFs Charge Transfer) The interaction between guest molecules and MOFs luminescence is mainly achieved through encapsulation of luminescent substances in MOFs materials, including rare earth ions, fluorescent dyes, quantum dots and other materials [17], so that MOFs materials have excellent luminescent properties.

3.3. Structural Stability

The interaction between the group and the open metal site Zn in the aqueous solution causes the deformation of the MOF composite system. The interaction between the two is mainly caused by electrostatic force, which leads to the significant increase of the interionic force. Due to the coulomb force between Zn-F atoms, the five-coordination four conical structure in Zn-MOFs is transformed into a six-coordination octahedron configuration, so as to achieve saturation coordination, so it has a stable structure [18].

4. Practical application scenarios of Zn-MOFs

4.1. Application in Medicine

In the past few decades, antibiotics have been widely used to treat bacterial infections in humans and animals [19]. The overuse of antibiotics has caused serious water pollution and a threat to public health. Therefore, it is very necessary to develop a convenient and effective method to detect antibiotic contaminants in water. Current detection methods mainly rely on capillary, electrophoresis, ion mobility spectrometry, mass spectrometer, Raman spectroscopy and other instruments for detection. However, these methods usually require highly trained technicians and complex equipment, which is time-consuming and expensive. At present, luminescent MOFs including Zn-MOFs, CD-MOFs, Zr-MOFs and lanthanide MOFs have been widely used in the detection of metal ions [20], organic small molecules [21], explosives, anions, antibiotics and fluorescent pH sensors. The fluorescence spectra of Zn-MOFs were significantly compared before and after the addition of various antibiotic solutions. Through the comparison, it was not difficult to find that the intensity of the fluorescence emission peak of Zn-MOFs was weakened to varying degrees after the addition of antibiotic solutions, that is, Zn-MOFs had certain fluorescence quenching effect in various antibiotic solutions. The fluorescence quenching effect of TC on Zn-MOFs was the strongest, and the quenching efficiency reached 92%. The results showed that Zn-MOFs could be used as an efficient fluorescence sensor to identify TC antibiotics in water. In order to further study the sensitivity of Zn-MOFs as a fluorescence sensor for TC detection in water, TC solution was gradually added into an aqueous solution with pH = 7.01 for fluorescence titration experiment. With the increase of TC concentration, the fluorescence intensity of Zn-MOFs was obviously quenched. Therefore, it can be seen that Zn-MOFs has great potential in the medical field [22].

4.2. Application in Nuclear Industry

At present, the treatment methods of radioactive wastewater include coagulation precipitation method,

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evaporation concentration method, membrane separation method, ion exchange method, biological method and adsorption method. However, most of these methods have certain disadvantages, such as precipitation method is easy to produce a large amount of sludge, photocatalytic degradation will produce some by-products, adsorption method has been widely used in radioactive sewage treatment due to its advantages of simple operation, low cost and easy large-scale application. In recent decades, researchers have been working on new adsorbents for radionuclides in water, including mesoporous materials, solid waste-derived adsorbents, covalent organic frameworks, graphene oxides, microorganisms and MOFs.

Metal-organic framework materials (MOFs), as a new kind of porous materials, are composed of metal ions or metal ion clusters bridged with various organic ligands. Compared with traditional porous materials, MOF materials have the advantages of large specific surface area, high porosity, diversified structure and functional adjustment, showing great application prospects in many fields such as storage drug transport, separation, catalysis and so on. Among them, the ZIFs (zeolitic imidazolate frameworks), mils (materials of institute Lavoisier), uios (University of Oslo) three MOFs materials skeleton structure will not collapse in the water, with a good stability. Much of the waste water produced by the nuclear industry is in a very low pH range. Zn-MOFs materials composed of zirconium ions and teraphenic acid or its derivatives are resistant to strong acid and moderate alkalinity. Zn-MOFs materials have attracted special attention of researchers and have been applied in the adsorption study of radionuclide U [23].

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