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Review

Luminescent nanoscale metal–organic frameworks for chemical sensing

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ABSTRACT

Metal–organic frameworks (MOFs) are a fascinating class of crystalline materials constructed from self-assembly of metal cations/clusters and organic ligands. Both metal and organic components can be used to generate luminescence, and can further interact *via* antenna effect to increase the quantum yield, providing a versatile platform for chemical sensing based on luminescence emission. Moreover, MOFs can be miniaturized to nanometer scale to form nano-MOF (NMOF) materials, which exhibit many advantages over conventional bulk MOFs in terms of the facile tailorability of compositions, sizes and morphologies, the high dispersity in a wide variety of medium, and the intrinsic biocompatibility. This review will detail the development of NMOF materials as chemical sensors, including the synthetic methodologies for designing NMOF sensory materials, their luminescent properties and potential sensing applications.

1. Introduction

Today, there is an increasing demand for chemical sensors to detect a variety of analytes for a range of applications, including environment monitoring, homeland security guarding, and food quality controlling. Typically, chemical sensors can bind selectively and reversibly the analytes of interest with a concomitant change in electrical, optical, or mechanical properties. Among all the chemosensors, luminescence-based ones present many advantages in terms of definite fluorescence spectrum, visible signal by naked eye, high sensitivity and selectivity, and ease of operation. Even so, there still remain great challenges to realize better sensory performance including increased brightness, higher quantum yield, excellent photo-stability under UV irradiation, and multi-functional systems. Here, a particular class of materials well-known as metal–organic frameworks (MOFs) will be presented to construct a robust platform to deal with these challenges.

MOFs, a promising class of hydrid materials constructed from straight self-assembly of metal cations/clusters and organic ligands through coordination bonds, have been extensively studied over the past two decades. The variety of metal and organic ligand building units makes it possible to prepare virtually unlimited MOFs to utilize many potential applications in numerous areas, including gas adsorption [1], separation [2,3], catalysis [4,5], chemical sensing [6–8], opto-electronics [9], clean energy [10], bio-imaging and drug delivery [11]. Among them, MOFs are utilized for chemical sensing mostly based on the fluorescence emission [12], because all of metal ions, organic ligands, metal–organic charge transfer, and luminescent guest molecules can generate luminescence [13,14]. And corresponding changes act in response to the uptake of analyte guests, as a mean of signal transduction. Furthermore, the functional sites in MOFs such as Lewis basic/acidic sites and unsaturated metal sites can be used for selective recognition of targeted molecules/ions. The tunable porosity can enable the reversible storage of guest species, making MOFs both as detection and pre-concentrator medium.

However, MOFs in the common form of bulk crystals cannot meet the specific requirements for analytical applications. In view of this, MOF materials are needed to be miniaturized at a nanometer scale or immobilized on selected substrates for practical applications. Nanoscale MOFs (NMOFs) have been proved to be a kind of effective sensory materials [15]. First, NMOF materials exhibit not only the rich diversity of compositions, structures, and properties as the bulk MOFs, but also the high dispersity in aqueous solution and the intrinsic biocompatibility, which facilitate the wide applications of NMOFs in the fields of chemical sensing [16,17]. Second, NMOF materials display extremely high surface areas to enhance the sensory performance

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in both response time and detection sensitivity due to a preconcentration effect, so the analytes are absorbed and concentrated inside the NMOF channels. The combination of nanoscale processability, intrinsic luminescent properties, and permanent porosity of NMOFs will definitely create a bright prospect for designing novel luminescent sensory nanomaterials with enhanced desired multifunctionalities.

2. Syntheses of luminescent nanoscale MOFs

Like macroscopic counterparts, NMOFs are mainly prepared through the "bottom-up" synthetic strategy based on straight self-assembly of inorganic and organic components. The synthesis of nanoscale metal–organic materials and porous materials has recently been reviewed [17,18], so general synthetic strategies for luminescent NMOFs are outlined. In order to clearly interpret various synthetic methods, these NMOF materials are classified into three broad classes: class I, direct luminescent MOF nanoparticles; class II, host NMOFs containing luminescent guests; class III, 2-dimension (2-D) NMOF luminescent films.

2.1. *Direct luminescent MOF nanoparticles*

Three different strategies are generally applied for synthesizing MOF nanoparticles: (i) the nano-precipitation method; (ii) the confinement at nanoscopic regime by using emulsions or templates; (iii) microwave or ultrasound assisted synthesis.

First of all, nano-precipitation is the simplest method for the preparation of MOF nanoparticles. This method usually involves two steps: (i) the dissolution of reaction precursors in a good solvent, (ii) the addition of a poor solvent to stop the assembly process, resulting in the formation of particles at a nanometer scale. Mirkin and Wang have done pioneering work to develop this methodology [19,20]. Lin applied this strategy to synthesize MOF nanoparticles constructed from the anticancer drug *c*,*c*,*t*-(diamminedichlorodisuccinato) Pt(IV) (DSCP) and Tb^{3+} ions [21]. Typically, a precursor solution of $TbCl_3$ (15 mmol) and DSCP (10 mmol) was mixed in H_2O, and the pH value was adjusted to 5.5. After that, methanol was rapidly added with vigorous magnetic stirring, which resulted in the formation of nanoparticles. However, this nano-precipitation method is not appropriate for crystalline NMOFs.

The second family of strategies for miniaturizing MOFs is the nanoscopic confinement effect assisted by surfactant. Lin developed a reverse microemulsion methodology to synthesize NMOFs, such as $Gd(BDC)_{1.5}(H_2O)_2$, $[Gd(BTC)(H_2O)_3]\cdot H_2O$ [22], and $Gd_2(BHC)(H_2O)_6$ [23]. Reverse microemulsions were formed by using surfactants to stabilize water droplets within a nonpolar organic phase. Two separate microemulsions containing either Ln^{3+} ions or organic linkers were mixed and reacted for a given period of time to form crystalline MOF nanoparticles. Eu^{3+} and Tb^{3+}-doped $Gd(BDC)_{1.5}(H_2O)_2$ nanorods were also prepared and proved to be luminescent.

The third family of strategies for miniaturizing MOFs is microwave or ultrasound assisted synthesis. Generally speaking, microwave irradiation can accelerate the crystal nucleation and produce nanocrystals with narrower size distributions than conventional solvothermal approach. Nanoscale Tb-MOF-76 was prepared through a rapid microwave-assisted method with proline and glycine as capping agents [24]. It exhibited a typical emission of Tb^{3+} ions, which was sensitive to acetone in aqueous solution. Similarly, ultrasonic irradiation can generate a homogenous nucleation and a substantial reduction in crystallization time. Well-defined Mg-MOF-74 nanocrystals with diameters of 100 nm were successfully synthesized in one hour in the presence of triethylamine as a deprotonating agent [25].

As for conventional solvothermal synthesis, various additives have been proved to suppress NMOF growth through a coordination modulation route. First, alkylamine additives such as triethylamine [25], *n*-butylamine and diethylamine [26] effectively deprotonate the metal complex and accelerate crystal nucleation, resulting in an obvious decrease of crystal sizes. Second, carboxylate and *N*-heterocycle additives, such as benzoic acid [27], acetate acid [28], sodium formate, sodium acetate [29], and 1-methylimidazole [30], have the same chemical functionality as the bridging linkers to impede the coordination interaction between the metal ions and the bridging linkers. Luminescent $Eu_{1-x}Tb_x$-MOFs nanocrystals around 100 nm were synthesized with the addition of sodium formate or sodium acetate, and further fabricated to form continuous films via spin-coating deposition [29]. The films exhibited strong luminescent properties and thus showed potential applications in the field of luminescent sensors. Other additives such as *p*-perfluoroethylbenzoic acid [31], dodecanoic acid [32], 4*n*-decylbenzoic acid [33] and polymers such as poly(acrylic acid sodium salt) [34] and poly(diallyldimethylammonium chloride) [35] were also used to control the sizes and morphologies of NMOFs.

2.2. *Host NMOFs containing luminescent guests*

Confinement of different guests, especially luminescent guests, into pores of NMOFs makes them versatile candidates to develop multifunctional sensory materials. One of the ideal methods is the direct incorporation of luminescent guests during the process of NMOF synthesis. Maspoch prepared metal–organic nanospheres constructed from Zn^{2+} and 1,4-bis(imidazol-1-ylmethyl)benzene (bix) by a fast precipitation [36]. These Zn(bix) nanospheres were used as functional matrices for the encapsulation of a variety of substances, such as luminescent quantum dots (QDs), fluorescein, rhodamine B, or two kinds of substances. The formed nanoparticles retained the intrinsic luminescent properties of guest species. Recently, a great breakthrough was the introduction of polyvinylpyrrolidone (PVP) as capping agents into the synthetic system of NP@MOF core–shell nanostructures [37]. A variety of PVP-capped nanoparticles (NP) was successively adsorbed on the continuously forming surfaces of ZIF-8 nanocrystals to form NP/ZIF-8 hybrid nanocrystals (Fig. 1). Imparting luminescent properties to ZIF-8 nanocrystals was demonstrated through separate encapsulation of lanthanide-doped $NaYF_4$ nanorods and CdTe QDs. Remarkably, the luminescent features of different cores were well maintained. Chi reported a highly-luminescent NMOF material

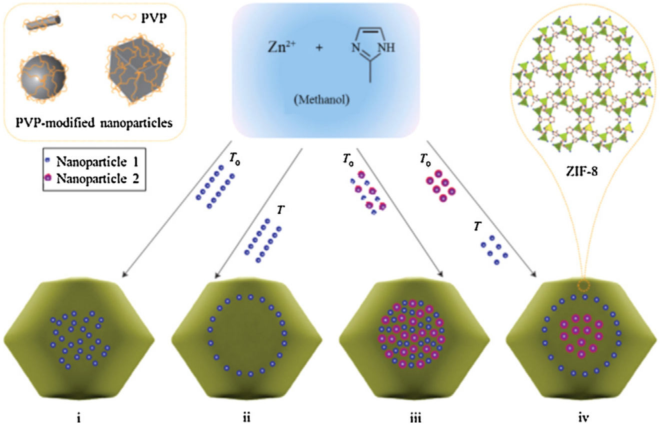

Fig. 1. Schematic presentation of the controlled encapsulation of various PVP-capped nanoparticles into ZIF-8 nanocrystals. Reprinted with permission from Ref. [37], Copyright 2012, Nature Publishing Group.