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Review

Recent progress in nanostructured magnetic framework composites (MFCs): Synthesis and applications

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ABSTRACT

The highly ordered porosity of metal organic frameworks (MOFs), constructed from different organic binding ligands and metal ions, render exceptional chemical and physical properties suitable for an array of applications in different domains. Recently, these materials have been employed to functionalize nanoparticles for the development of magnetic framework composites (MFCs). This fascinating class of MOFs aims to amalgamate the intrinsic properties of MOFs with the benefits of magnetic property to further accentuate their performance and broaden the applications. Specifically designed MFCs offer novel properties such as devisable composition, large surface area, easy loading and rapid collection. This review presents a holistic insight into efficient strategies for fabricating MFCs such as non-core-shell and core-shell methods. Further, the recent progress of MFCs in the areas of separation/treatment processes for dye, heavy metal, pollutants from a variety of wastewater is exploited. In the field of catalysis, MFCs not only act as photocatalysts but also provide a platform for utilizing noble metals and enzymes. This facilitates their easy separation from the reaction mixture. Effort is warranted in providing a balanced outline of the application of MFCs for extraction and biomedical applications.

1. Introduction

Metal organic frameworks (MOFs) are a vibrant class of ultraporous hybrid material with virtually large crystalline structures composed of inorganic and organic units linked *via* coordination bonds. MOFs have developed rapidly and gained tremendous attention due to their versatile nature, diverse and highly-ordered structures, ease in functionalization and high stability (chemical and thermal) [1–3]. These structures possess large surface area (more than 2,000-8,000 m^2 g^{-1}) [3–5], high porosity, well–defined channels, availability of in–pore functionality and flexibility owing to their structural and chemical tenability. Also, it allows systematic engineering and modification of chemical and physical properties of MOFs by selecting appropriate metal centers, ligands, and synthetic conditions to get precise pore size and spatial cavity arrangement for specific applications [6–8]. When compared with conventional porous materials (such as alumino-phosphates, metal oxides and mesoporous silica materials), certain MOFs (generally zeolite-like metal–organic frameworks) can be easily generated through sustainable methods under gentle synthetic conditions, resulting in highly crystalline materials, which are ideal for exhaustive determination of their structures [9,10]. In the last

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Abbreviations: AEAPTMS, N-(3-(Trimethoxysilyl)propyl) ethylenediamine; AOP, Advanced Oxidation Processes; APTES, (3-Aminopropyl)triethoxysilane; H2BDC, Benzenedicarboxylic Acid; BET, Brunauer, Emmett and Teller; BJH, Barrett–Joyner–Halenda; BSA, Bovine serum albumin; BTC, Benzene-1,3,5-tricarboxylic acid; CalB, Candida Antarctica lipase B; CP, Chlorophenols; DFT, Density Functional Theory; DMF, Dimethylformamide; DMSO, Dimethylsulfoxide; DOTA, ZIF-; DOX, Doxorubicin; DUT, Durban University of Technology; EDC, 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide; EDTA, ethylene diamine tetra acetic acid; GA, Gallic acid; GO, Graphene Oxide; GOx, Glucose oxidase; HAADF-STEM, High angle annular dark field-scanning transmission electron microscopy; HKUST, Hong Kong University of Science and Technology; HRP, Horseradish Peroxidase; ICP, Inductively Coupled Plasma; IRMOF, Iso-reticular MOFs; LED, Light Emitting Diode; M-MOF, Magnetic–MOF; MALDI, matrix-assisted laser desorption/ionization; MB, Methylene Blue; MFC, Macro Fiber Composite; MIL, Materials Institute Lavoisier; MNP, Magnetic Nano Particles; MO, Methyl Orange; MOF, Metal Organic Frameworks; MPC, magnetic porous carbon; MR, Magnetic resonance; MSPE, magnetic solid-phase extraction; MWCNT, Multiwall Carbon Nanotubes; MWCT, ; NHC, nanoporous hybrid carbon; NHS, N-hydroxysuccinimide; NIR, near infrared; P4VP, Poly(4-vinylpyridine); PAH, Polycyclic Aromatic Hydrocarbons; PDA, Polydopamine; PSMR, Post-synthetic Modifications Routes; PSS, Poly(sodium 4-styrenesulfonate); PVP, Polyvinylpyrrolidone; RhB, Rhodamine B; SCE, Saturated calomel electrode; SEM, Scanning electron microscope; SPE, solid-phase extraction; TMB, Tetramethylbenzidine; UiO, University of Oslo; XRD, X-ray Diffraction; ZIF, Zeolitic Imidazolate Framework.

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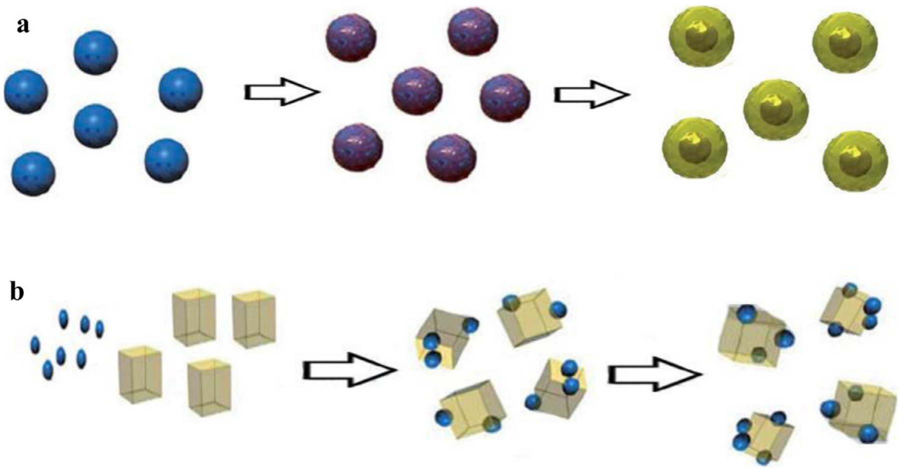

Fig. 1. The design of magnetic framework composites. (a) core-shell MFCs and (b) non-core-shell MFCs.

decade, more than twenty thousand different MOFs have been synthesized which have shown enormous potential in an array of applications in the field of catalysis, gas storage, separation, drug delivery, electronic/opto-electronic devices and sensors [11–15].

Although ample literature is available on the development of MOFs and their application, recently, nanomaterial integrated MOF composites have come up as a new research trend and have raised broader interests. A variety of nanoparticles (such as quantum dots, metal nanoparticles/nanorods, multiwall carbon nanotubes (MWCNT), graphene and porous silica nano-sphere) are combined with MOFs and their performance characteristics are assessed in the areas of sensing, optics, catalysis, drug delivery and environment remediation. This sophisticated architecture of MOF composites exhibits enhanced/new physicochemical properties as compared to their pristine counterparts [12]. Among the various nanomaterial MOF composites, multifunctional magnetic hybrids have been a sought after topic. This is because they possess both the magnetic properties of metal or metal oxides (mostly Fe_3O_4) and the diverse functions of MOFs in one material. The presence of magnetic nanoparticles has dual advantages. Firstly, it eases the separation process. They avoid the need of laborious high-speed centrifugation or filtration separation after use [17]. Secondly, it improves the thermal stability of formed MFCs as compared to plain MOF (without magnetic nanoparticles) [18]. This is due to the presence of dispersive forces within the MOFs, which suppress their aggregation and control the structure, morphology, and size of MOFs which ultimately augments physio-chemical properties [13,14].

This review covers the scientific development and progress in the field of magnetic framework composites (MFCs). Further, various strategies of the manufacture of magnetic framework materials have been elucidated. At the end, various applications of these MOFs in different fields, including domains of biomedical, solid phase extraction, catalysis and many more have been reviewed.

2. Types of magnetic framework composites

Magnetic framework composites have been classified here as core-shell and non-core-shell type based on their structure (Fig. 1). Various techniques can be engaged for the synthesis of both these types of MFCs. The MFCs synthesized by *in situ* method and embedding technology are of the non-core-shell type [19,20]. Here, the magnetic nanoparticles are secured/fixed on the outer surface of the pre-synthesized MOF or solvothermally synthesized within MOFs. In core-shell preparation, 'functional' magnetic nanoparticles act as the core material and the shell is a feedstock material of the MOF. Under controlled conditions, organic precursor and ligands rapidly form the shell, and grow the network of MOF around the core MNPs. The different preparation methodologies of MFCs are described below:

2.1. Core-shell MFCs

Encapsulation is one approaches for synthesis of core-shells MFCs in which magnetic materials are functionalized/coated (with a polymer or a carbonaceous layer) to trap material with better compatibility. Thereafter, the nanocomposites are added for initial nucleation and growth along with various counterparts. The interface between magnetic particles and the porous framework help to grow MOF around the carrier and MFCs are prepared. Ke and co-workers prepared core-shell Fe_3O_4@MOF by using mercaptoacetic acid (MAA)-functionalized Fe_3O_4 nanospheres and H_3BTC [21]. An advanced and rapid MFCs method for the synthesis was recently demonstrated by microfluidic device. Kim and team used microreactors (made up of microdroplets) for the production of MFC in a very quick time. Here, the magnetic Fe_3O_4 nanoparticles were coated using a polystyrene sulfonate as a buffer interface which was further successfully encapsulated into ZIF-8 [22].

Layer by layer is another method for preparation of MFC in which the functionalization on the MNP is used to grow the shell of MOF around them. In this method, ligands (bi/trivalent metal ions) and inorganic precursors (most commonly, nitrate or acetate salts) are combined with the functionalized particles in a solvent or mixture of solvents. Solvothermal or hydrothermal processes can be opted for, depending on the type of solvent being used. In this nanocomposite, the MOF is grown layer-by-layer to form the MFC structure [23,24]. There are three ways of functionalization of MNPs (Fig. 2) - (i) Simultaneous synthesis and functionalization of MNPs in one step (ii) synthesis of bare MNPs and then coating them with functionalizing agents, and (iii) synthesis and consecutive linking with an encapsulating agent. Generally, carboxylate, phosphonate, thiol, and hydroxyl functional groups can bind to the surface of MNPs. The list of the different functionalizing agents is given in Table 1. The colloidal stabilization of the MNPs has been done by citrate and other small molecules. These molecules may be adsorbed on the surface of the MNPs *via* formation of coordination bonds. These bonds rely on the curvature of the surface and steric character of the functionalities [25]. In a remarkable example, Lu and co-workers used polyvinylpyrrolidone (PVP) coated magnetic nanoparticles for the controlled growth of

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