Cyclodextrin Metal?Organic Frameworks (MOFs)

Cyclodextrin Metal?organic frameworks (MOFs) were emerged as a new class of nanoporous materials and with wide range of applications in molecular recognition, gas storage, catalysis, and drug delivery aspects. Generally, they were constructed with metal ion connectors and with organic bridging ligands. Naturally for conventional porous materials, the pore size and inner surface characteristics of MOFs were modulate by tuning the size and shape of the linkers (Bigdeli, M. and Morsali, 2015).

The sizes and shapes of MOF materials were main criteria for various applications. Therefore, many efforts were directed to shorten the synthesis time for production of uniform crystals by using microwave-assisted, mechanochemical, and sonochemical methods. Several strategies were adopted for controlling the size and morphology of MOFs by altering the synthetic parameters includes temperature, processing duration, metal source, and solvents. Ban et al. (2013) reported the morphologically controlled synthesis of ZIF78 materials by altering the nutrients and ligands concentrations. Pan et al. (2011) in his studies demonstrate about facile synthesis method using cetyltrimethylammonium bromide as a capping agent for controlling the size and morphology of ZIF-8 crystals in aqueous systems. The Solvothermal method for the controlled synthesis of NH2-MIL-53 was altered by DMF and water ratios without mixing of surfactants or capping agents (Cheng et al., 2013).

In recent years, industrial, pharmaceuticals, and food processing interests shifts towards encapsulation of drugs in MOFs due to its varied applications. However, it was necessary to consider the biocompatibility of the material compositions for different types of MOF. Appropriate natural molecules like amino acid, peptides, and nucleobases, were considered as well known metal ions (Ca, Mg, Zn, Fe), and were considered to be biocompatible as organic linkers and metal network connections of MOFs, respectively. Functionalized linkers of postsynthetic modifications which were biofriendly show their advantages over other reactive groups in various structures of MOFs (Bonnefoy, J et al., 2015).

The MOF prepared through kneading method was suitable for poorly water-soluble guests, due to the guest molecules dissolves slowly during the formation of MOF (Marques, HMC, 1994). It provides good yield formation of MOF but it was not suitable for large scale preparation (Daletos G et al., 2008). The liquid or dissolved solid guest was added to slurry of cyclodextrin and kneaded (in a mortar), and then the paste is dried. The obtained solid was washed with methanol solution to remove the debris which were adsorbed on the cyclodextrin surface. The sample was then dried under vacuum to remove excess moisture. The inclusion complex formation of cyclodextrins by kneading method has been reported in the encapsulation of ibuprofen, omega-3 fatty acids in thymol essential oil, thyme essential oil and European anchovy (Engraulis encrasicolus L.) oils.

The MOF prepared through co-precipitation method was useful for non-water-soluble substances. This method was not effective and gives Poor yield due competitive inhibition from organic solvents used as the precipitant (Hirayama F and Uekama K, 1987). The guest molecules was dissolved in organic solvents like chloroform, benzene and diethyl ether, etc, and appropriate amount of cyclodextrin which can dissolve in water was added with agitation. The solution was then cooled and complex crystals were formed. The crystals which were formed was wash with organic solvent like absolute ethonal or methanol and then dried at 50°C to remove excess moisture (Saenger W, 1980). The co-precipitation technique was applied for the encapsulation of drugs such as oxaprozin, and trans-anethole.

The MOF prepared through the freeze-drying technique is suitable for thermolabile or water soluble guests (Saenger W, 1980). Cyclodextrin and the KOH molecule were dissolved in water in required proportions by stirring. The solution was then freeze-dried and the obtained small powderlioke crystals was washed with organic solvent and then dried under vacuum (Junco S et al., 2002). This method produces good yield of inclusion complex. Comparing with knending and co-precipitation techniques freeze-drying technique has been wildly useful for cyclodextrin inclusion complex formation, especially water soluble hydroxyproply-?-cyclodextrin.

Stoddart et al. (2010) reports the vapour diffusion method by synthesis of environmentally friendly and renewable cyclodextrin metal?organic frameworks (CD-MOFs).The CD-MOFs were body-centered cubic extension like structures, prepared by the coordination of CD and potassium ions and possesses large spherical voids of 17 Å with apertures of 7.8 Å. CD-MOFs were the materials having more potential than any other MOFs so far, and have the capability to adsorb gases like N_2, H_2, CO_2, and CH_4 and some other molecules like Rhodamine B and 4-Phenylazophenol through encapsulation process (Smaldone, 2010).

Taking advantage of their uniform channels (17 Å) and high local concentrations of OH? ions, the CD-MOFs were used as template for the synthesis of silver and gold nanoparticles (Wei et al., 2012). The CD-MOFs with vapor diffusion method was able to produce cubic crystals of range 40?500 ?m at ambient temperature over the period of 7 days. A modified method with the mixture of CTAB in ambient temperature with controlled incubation time for 26?32 h CD-MOF produces crystals, due to this method good quality crystals were achieved with well-defined shape in the range of several hundred nanometers to millimetres (Furukawa, Y et al., 2012). But, the vapor diffusion method was very difficult for fabrication and mass production which was useful for industrial purposes. The CD-MOFs produced through vapourdiffusion method with mixture of CTAB shows quite toxic for cells.

The majority of Metal Organic Framework crystals have been prepared by solvothermal synthesis which requires days to weeks to produce MOF crystals. To overcome this limitations microwave assisted method was explored. Microwave assisted procedure involves the use of microwave irradiation, which was energy efficient internal heating by direct coupling of microwave energy with dipole and ions present in the recent mixture. Microwave irradiation achieves extremely fast heating rate on the target resulting in faster reaction with in short period and suppressing the formation of by-products and higher product yields.

The reaction time is shorter in mictowave-assisted method and hence, the kinetics crystal nucleation and growth was much faster than the conventional methods. The fabrication of cyclodextrin Metal organic Framework crystals was carried out by microwave assisted method (Liu et al., 2017). A mother solution was with pre-adition of methnol, which was sealed and placed in glass vessel. The solution was heated heated at 40~100 0C in microwave synthesizer with 100watt power to get clear solution after 1~120 min. Polyethylen glycol (PEG) was used to trigger the crystal formation.