

Sonochemical synthesis of fabrication nano porous metal-organic framework base on tetrakis(4-carboxyphenyl) porphyrin (TCPP) linker

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Abstract

Crystal engineering the design and synthesis of supramolecular metal-organic frameworks is frontier field in research, not only for their variety of architectures and interesting molecular topologies but also because of their potential applications in zeolite-like catalysts, host-guest chemistry, gas storage, ion exchange, molecular recognition, photonic materials and magnetic. High quality crystals of metal-organic coordination compounds, such as those suitable for single-crystal X-ray diffraction measurements, can usually be obtained by a variety of approaches using wet solution chemistry solvothermal methods. High-energy ultrasound irradiation has been used for the synthesis of a zinc(II) MOF, $Zn_2(Zn_TCPP)_3H_2O \cdot 2DMF$ (**1**), (TCPP) = tetrakis (4-carboxyphenyl) porphyrin in nano scale. The nano-structure was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRPD), FTIR and elemental analyses. The utilization of high intensity ultrasound has found as a facile, environmentally friendly, and versatile synthetic tool for the coordination compounds.

Keywords: Metal_organic framework (MOF), porphyrin, sonochemical

Introduction

In recent two decades, metal-organic frameworks (MOFs) have received tremendous attention due to their powerful attributes on structural and chemical versatility and tailor ability[1]. Metal-organic frameworks (MOFs) are a class of highly tunable, porous molecular materials with properties suitable for a wide variety of applications, including gas storage separation, catalysis, nonlinear optics, sensing and imaging, drug delivery, and others[2]. In nature porphyrins are well known for performing many biological functions in aqueous media, such as light harvesting, oxygen transportation, and catalysis[3]. most of MOFs have been generally prepared in a powder form However, MOF-Porphyrin highly porous, MOFs are preferred in many applications in order to fully employ their outstanding properties[4].

Experimental

A mixture of $Zn(OAc)_2 \cdot 6H_2O$, meso-Tetra(4-carboxyphenyl) porphyrin N,N-dimethylformamide and ethanol was respectively, were added to a basher and sonicated. The obtained precipitates were filtered off, then washed with DMF. was positioned in a high-density ultrasonic probe at ambient temperature and atmospheric pressure, operating with a power output of 12 W [5-6].

Results and discussion

SEM, FT-IR and XRD analysis.

XRD patterns of the MOF-Porphyrin were measured by an X-ray diffractometer(XRD). The morphologies of MOF-Porphyrin were investigated by a scanning electron microscopy (SEM) and FTIR spectra.

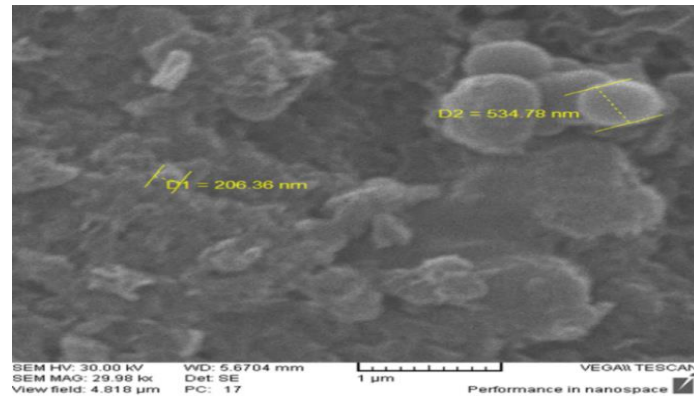


Fig.1: scanning electron microscopy (SEM) MOF-Porphyrin

Discussion Scanning electron microscopy (SEM) analysis clearly exhibited the formation of a Structure process. The obtained Zn MOF-Porphyrin an average diameter of approximately 205 nm and a length of 500nm. A light surface was changed to dark purple after the chemical treatment in the H₂TCPP solution, suggesting the formation of a Zn-based MOF. In the resolution SEM image of the resultant MOFs look like a surface morphology. In the magnified in set, however, the crystals clearly display with a diameter, being consistent with the morphology of Cu-TCPP MOFs reported by Rahimi [5].

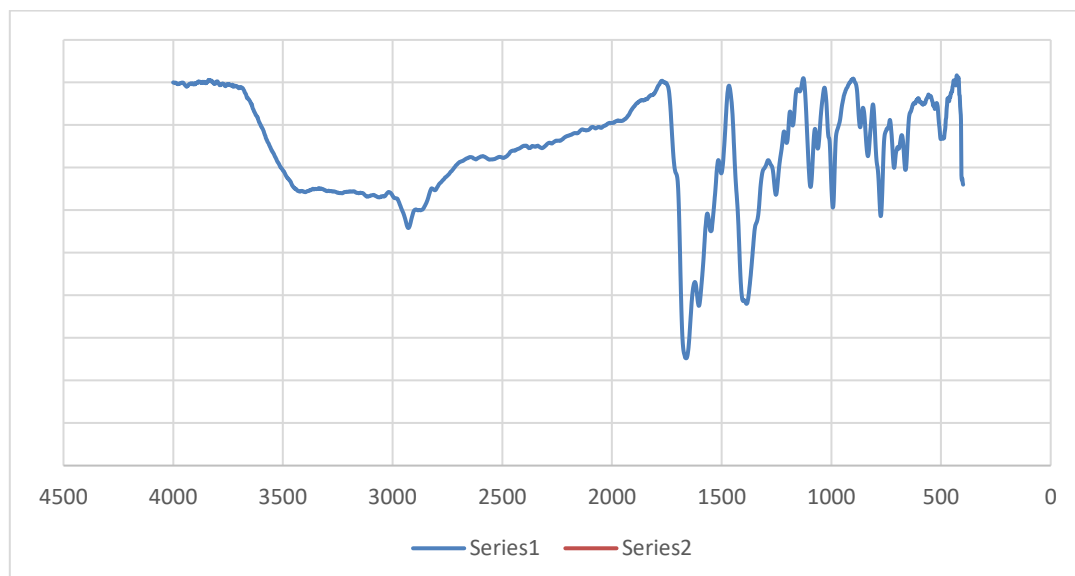


Fig.2: FT-IR spectra MOF-Porphyrin

Fourier transform infrared spectra were recorded by a FTIR-8400S spectrophotometer (Shimadzu, Japan) in the range of 400-4000 cm^{-1} . The FT-IR spectra of TCPP and Zn–TCPP MOF are shown in (a strong C=O stretching band can be observed at approximately 1700 cm^{-1} in the FTIR spectrum of pure TCPP. Zn–TCPP MOF and prepared shows an almost vanished peak around 1700 cm^{-1} and two new peaks at 1620 and 1400 cm^{-1} , which indicates the coordination of the carboxyl group in TCPP to the Zn atom[8].

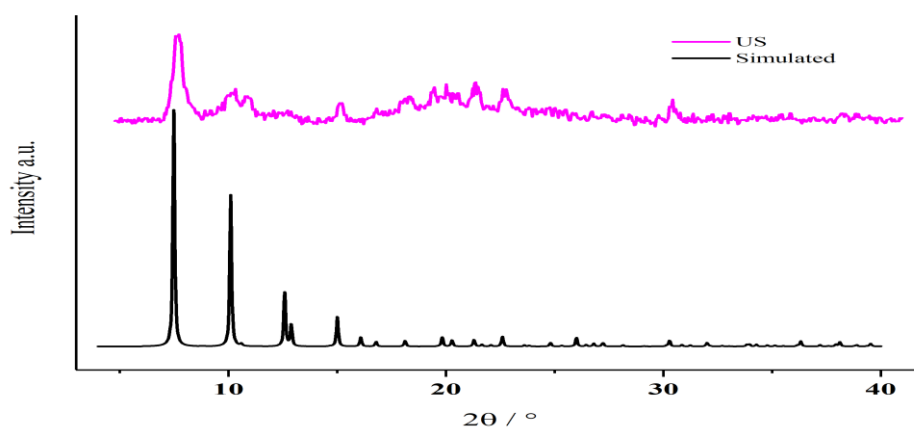


Fig.3: XRD patterns of the MOF-Porphyrin

The X-ray powder diffraction was recorded by an XRD diffractometer (Philips X' pert, Netherlands) equipped with Cu α radiation ($\lambda = 1.5406 \text{ \AA}$) in a 2θ range of $5^\circ \leq 2\theta \leq 80^\circ$. The surface areas of the materials were determined using The XRD patterns of the MOF-Porphyrin, are shown in pattern. All the diffraction . other impurity peaks were detected . The XRD patterns of prepared Zn-TCPP MOF is identical to that reported in the literature, verified the correction of MOF synthesis. The highly ordered in-plane molecular arrangement in Zn-TCPP MOF consists of a "checkerboard" motif of Zn-centered TCPP units linked by binuclear $\text{Zn}_2(\text{COO})_4$ paddle wheels. In the XRD patterns of the prepared MOF all of the reflections could be indexed as (hkl) of the pseudo-2D tetragonal unit cell [9-10].

Conclusions

In this study, MOF-Porphyrin constructed from free-base porphyrin linkers and Zn nodes were grown on conducting glass substrates by using a sonochemical approach. The obtained Zn MOF-Porphyrin, $\text{Zn}_2(\text{ZnTCPP})_3\text{H}_2\text{O} \cdot 2\text{DMF}$, is assembled from the metal containing ligand Zn-tetra-(4-carboxyphenyl) porphyrin (ZnTCPP), which is connected by Zn paddlewheel clusters, $\text{Zn}_2(\text{COO})_4$, as inorganic secondary building units. The structure ZnTCPP and paddlewheel cluster form a 2D square grid. These grids are stacked in packing pattern. As a result, the porphyrin zinc atoms are arranged in line with the paddlewheel zinc atoms. Solvent water molecules coordinate to zinc atoms in both the Zn paddlewheel cluster and ZnTCPP.

Interestingly, the zinc atom in TCPP is disordered as slightly above or below the porphyrin plane. The 2D porphyrin layer forms square channels with dimensions of approximately $11.8 \times 11.8 \text{ \AA}$ along the direction. Despite the existence of such open channels, the structure is not interpenetrated, unlike other paddlewheel frameworks.

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