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Mechanical Synthesis of Zn-HKUST-1 Metal-Organic Framework and Investigation its Fluorescence Sensing Ability Toward to Detect Explosive-like Nitro aromatic Analytes Such as TNT

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Abstract

Metal-Organic Framework (MOFs) are new crystalline materials which because of having properties such as high porosity, optical and electrical properties, etc., have been considered in areas such as gas storage, catalysis, pollutants removal and so on. Therefore, in order to develop these compounds and their use in this study, in this work, Zn-HKUST-1 metal-organic framework was synthesized by fast and also environmentally friendly physical mixing (grinding by hand) method. To identify products spectroscopy methods such as FT-IR and PXRD were employed. The sensing ability of this framework to detect explosive-like nitroaromatic analyets such as nitrobenzene, 1,3-dinitrobenzene and TNT was tested. The results showed that the sensitivity of Zn-HKUST-1 to TNT is more than two other analytes and this metal-organic framework can be effective in detecting explosives such as TNT. Also ultrasound assisted synthesis (sonochemical) of this framework and effect of initial reagents concentration and power generating ultrasonic apparatus on the size and shape of the products were investigated.

Keywords: *Metal-Organic Framework (MOFs), Mechanochemical, TNT, X-ray Crystallography.*

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Introduction

In the last decade, metal-organic frameworks (MOFs) have received considerable interest due to their potential applications in different fields such as catalysis, gas storage and sensing [1-3]. This interest is largely based on the ability to tailor the topology, pore size and functionality by judicious selection of the molecular building blocks [4]. Taking advantage of this feature, many chemists have tried to design various MOFs with desirable structures and properties. The selective molecular recognition and sensing of small molecules by MOFs have been identified as one of the important and exciting area of research in the recent few years [5-6]. Much attention has been focused on sensing and removal of toxic chemicals, such as nitroaromatic compounds (NACs) [7-9], small aromatics [10-11] and polycyclic aromatic hydrocarbons (PAHs) [12-13].Recently, it has been proposed that the aromatic organic ligands in the MOF structure play an important role in interacting with NACs via π-interactions, namely π-π stacking and C-H$\cdots\pi$ interactions [14].

Nowadays, an increasing number of investigations have focused on the design and construction of MOFs with specific morphologies, as the size and shape of this novel type of nano/microscale materials arevery important for their different applications in gas storage, diagnostics,sensing, catalysis, ion exchange or separation, and optics [15-16]. Recentadvances in nanostructured MOFs have been led by developmentof new synthetic methods that provide control over size, morphology,and nano/microstructure [17].

Among the various nanostructures,one-dimensional (1D) nanoscaled MOFs, such as nanowires, nanorods,and nanotubes, have been regarded as significant factors thatmay influencethe chemical and physical properties and bring wide applications[18]. Over the past decade, utilization of ultrasound for nanomaterial synthesishas been grown at an enormous rate, and is nowpositioned asone of the powerful tools inmetal–organic framework synthesis [19-20]. Ultrasound causes high-energy chemistry. It does so through the processof acoustic cavitation, which includes formation, growth, and implosivecollapse of bubbles in a liquid medium. A bubble can overgrowand subsequently collapse within a very short lifetimes ($> \backslash\cdot^{\backslash\cdot}$ K s^{-1}).A large energy concentration is achieved during the collapse, resultingin a local temperature of ~5000 K and a pressure of ~1000 bar [21].

Utilizationof high intensity ultrasound offers a rapid, mild, cost-effective, reproducible,and environmental friendly growth strategy for nano/microscaledcoordination complex compounds with novel morphologies and uniqueproperties [22].In this work Zn-HKUST-1 metal-organicframework was synthesizedby fast and also environmentally friendly physical mixing (mechanical grinding)

methodand was studied the ability of this MOF to sense aromatic explosive compounds. Also ultrasound assisted synthesis of this framework and effect of initial reagents concentration and power generating ultrasonic apparatus on the size and shape of the products were investigated.

Experimental

Materials and physical techniques

ExceptTrinitrotoluene (TNT) that was synthesized, all reagents and solvents for the synthesis and analysis were commercially available and were used as received.Powder X-ray diffraction (PXRD) of compound was carried out on a diffractometer of Philips Company with X'pert monochromatized Cu kα radiation. Simulated XRD powder patterns were calculated using Mercury based on the single crystal data. FT-IR spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500–4000 cm^{-1} using the KBr disk technique.Ultrasonic generator was carried out on a TECNO-GAZ, Sonicator-3000.The samples were characterized by field emission scanning electron microscope (FE-SEM) SIGMA ZEISS and TESCAN MIRA (Czech) with gold coating.The Fluorescence properties of Zn-HKUST-1 were measured in different solvent emulsions containing MOF using a PerkinElmer-LS55 Fluorescence Spectrometer at room temperature.Time-dependent density functional theory (TD-DFT) calculations were performed using GAMESS suite of program [23].

Mechanical Synthesized of Zn-HKUST-1

Zn-HKUST-1 was synthesized by grinding $Zn(OAc)_2 \cdot 2H_2O$ (1mmol), and H_3BTC (0.75mmol) by hand for 30 minutes. The resulting powder was washed with small amounts of DMF in order to remove any unreacted starting material. The product was heated at 100°C for 8 h beforeand after washing with DMF(yield: 70%).For activation, the product was heated at 120 °C for 12 h after washing with DMF, m.p. > 350 °C, (This process are shown in Figure 1).
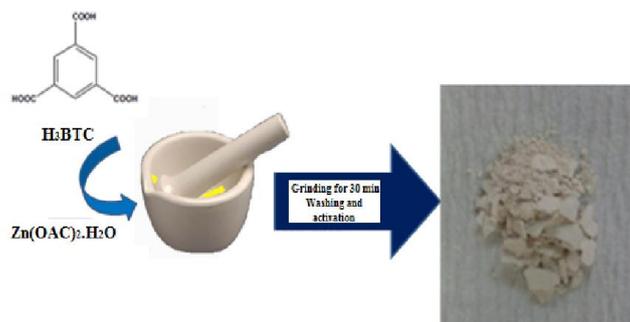
Figure 1. Mechanical synthesized of Zn-HKUST-1 powders.

Sonochemical Synthesis of Zn-HKUST-1

To prepare nano-sized Zn-HKUST-1, 12.5 ml solution of zinc(II) acetate dehydrate (0.02 M) in DMF was positioned in a high-density ultrasonic probe, operating with a maximum power output of 12 W. Into this solution 12.5 ml solution of H_3BTC (0.013 M) in DMF was slowly added. After 30 minute, obtained precipitates were filtered off, washed with DMF and then dried in air, m.p. > 350 °C.

Fluorescence Measurements

The Fluorescence properties of Zn-HKUST-1were measured in different solvent emulsions containing MOFs using a PerkinElmer-LS55 Fluorescence Spectrometer at room temperature. In a typical procedure, 1 mg of an activated MOF was grinded down, and then immersed in different analyte solutions (4 ml) and after 24 hours was tested in the emission mode.

According to the Stern-Volmer equation;$(I_0/I)= K_Q [A] + 1,$ Where here, I_0 is the initial fluorescence intensity of soaked MOF sample in toluene, I is the fluorescence intensity in the presence of analyte, [A] is the molar concentration of analyte, and K_Q is the quenching constant (M^{-1}). For the quenching constant extraction, emission intensity of MOFs was recorded by suspending them into different concentrations of analyte solutions in toluene, upon the same manner described in Fluorescence measurement section.

Result and discussion

Zn-HKUST-1 ([$Zn_3(BTC)_2(H_2O)_3$], where BTC = 1,3,5-benzenetricarboxylate),is a Zn analogue of Cu-HKUST-1 with *tbo* net topology, made with the small and rigid tricarboxylate, BTC, as an organic component. The hydrothermal reaction of zinc(II) nitrate hexahyradate with 1,3,5-

benzenetricarboxylate in 1:0.75 mole ratio at 85 °C for 72 h yields colorless crystals of Zn-HKUST-1, which is suitable for X-ray crystallography. In a facile and environmentally friendly synthesis method, Zn-HKUST-1 was synthesized by the mechanochemical reaction(grinding by hand) of a mixture of Zn(OAc)$_2$.2H$_2$O and BTC ligand in molar ratio 1:0.75for 30 minutes.Compared with conventional heating synthesis of the compound Zn-HKUST-1, mechanochemical synthesis is found to be a highly efficient method.

The simulated (derived from the single crystal structure of MOFs), the single crystal MOF as synthesized and experimental (resulting from the mechanical synthesized powder) powder X-ray diffraction (PXRD) patterns are consistent (Figure 2a), confirming that the mechanical synthesized powders were structurally identical to samples that prepared *via* conventional heating. The FT-IR spectra of the powders produced by the mechanical synthesized method and of the crystals material are indistinguishable (Figure 2b).

The spectrum of as-synthesized and grinding samples Zn-HKUST-1 are dominated by the vibrational modes of the BTC linker. In particular, the IR absorption bands in the 1700–1500 cm^{-1} and 1500–1300 cm^{-1} ranges are due to $\upsilon_{asym}(C–O_2)$ and $\upsilon_{sym}(C–O_2)$ stretching mode, respectively; IR bands around 1440 cm^{-1} are due to a combination of benzene ring stretching and deformation modes; whereas, IR absorption bands around 700 cm^{-1} are due to $\upsilon(C–H)$ bending mode.
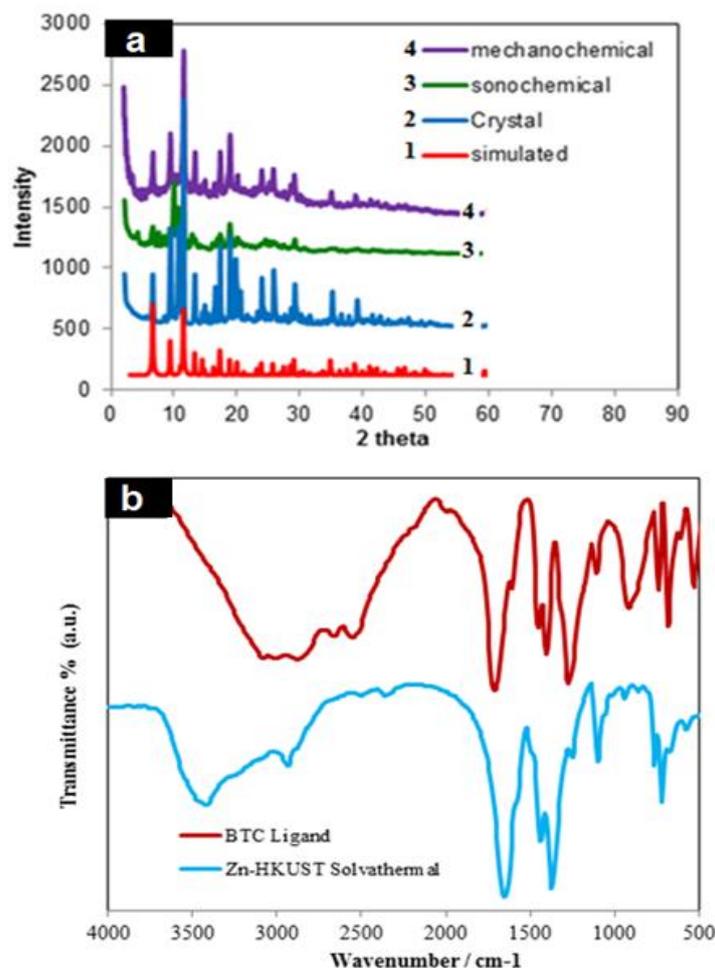
Figure 2. (a): PXRD patterns of simulated (1), as-synthesized (2), sonochemical (3) and mechanical synthesized (4), of Zn-HKUST-1 (b) FT-IR spectra of BTC ligand (red) and Zn-HKUST-1framework (blue).

Since the composition of Zn-HKUST-1framework has countless number of aromatic benzene rings, this framework may be good candidate for fluorescence sensing study. Zn-HKUST-1 has an absorption band at 340 nm and exhibits strong fluorescence at 380 nm upon excitation at 340nm.The observed fluorescence intensity may be due to the different measurement conditions such as solvents, source lamp intensity ofFluorescence Spectrometer and etc. The fluorescence properties of Zn-HKUST-1 were preliminary evaluated by immersing the activated MOF in three aromatic solvents, benzene, toluene and nitrobenzene, (Figure 3a).
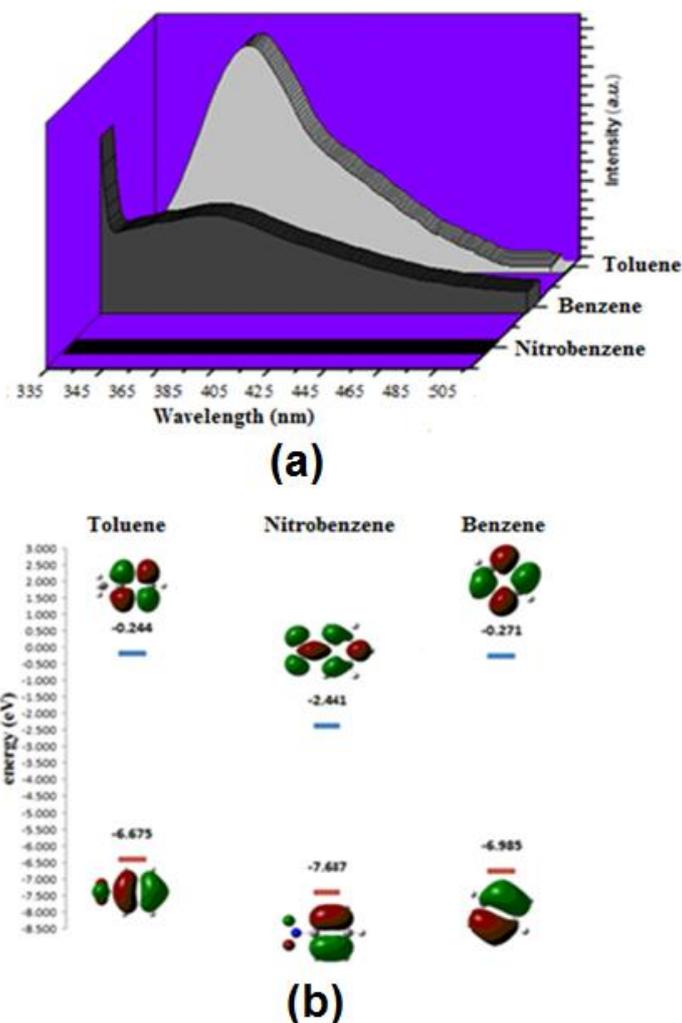
Figure 3. (a): Fluorescence emission spectra of Zn-HKUST-1 dispersed in nitrobenzene, toluene and benzene, (b): HOMO and LUMO of toluene, nitrobenzene, benzene.

Notably, this MOF exhibit almost complete fluorescence quenching when immersed into nitrobenzene, with the quenching efficiency of more than 98% for both MOFs. Also, the quenching efficiency follows the order of toluene<benzene<nitrobenzene, which is in agreement with electron-withdrawing ability of the substituent group on aromatic ring.

To understand the fluorescence quenching behaviors of Zn-HKUST-1, the frontier Molecular orbitals of benzene, toluene and nitrobenzene were calculated using time-dependent DFT (TD-DFT) calculations (see computational details). As depicted in Figure 3b, the LUMO (-2.441 eV) of nitrobenzene lies at lower energies as the LUMO of benzene (-0.271 eV) and toluene (-0.244 eV). The results suggest that photo-induced electron-transfer (PET) mechanism may be responsible for

fluorescence quenching, since the order of quenching efficiency is identical to the order of the LUMO level energies.

To understand the quenching effect of nitrobenzene in detail, the Stern-Volmer (SV) quenching plot is constructed by monitoring the fluorescence intensity of Zn-HKUST-1 in the presence of different concentration (50-2000 ppm) of nitrobenzene, (Figure 4a). The plots display a linear response with a Stern-Volmer quenching constant (K_Q) of606.2 M^{-1} for Zn-HKUST-1, (Figure 4b).The PET mechanism could be further confirmed by observing the following: i) linear SV behavior ii) No overlapping between the absorption band of nitrobenzene and the emission band of the Zn-HKUST-1 framework. Thisresult implies that the Zn-HKUST-1 can recognize this explosive-like nitroromatics by fluorescence sensing because of that fluorescence intensity quenching of this framework in the presence of high concentration of nitrobenzene is faster and more effective compared to that of lower concentration.
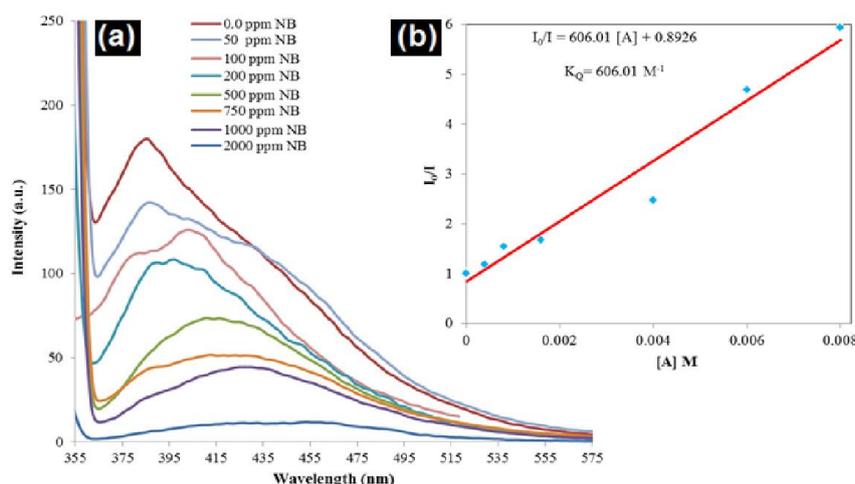

Figure 4 (a):Fluorescence emission spectra ofZn-HKUST-1 in the presence of different concentrations of nitrobenzene, (b) Stern–Volmer (SV) plots in the presence of 1 mg of Zn-HKUST-1 in different nitrobenzene concentrations ([A]) in toluene.

These results encouraged us to further evaluate the sensing ability of Zn-HKUST-1 towards other nitroaromatic compound, namely 1,3-dinitrobenzene that have one more electron deficient NO_2 group. Thus, fluorescence quenching experiments were carried out using three different concentrations (100, 200 and 300 ppm) of 1,3-dinitrobenzene in toluene solvent. As shown in Figure 5, fluorescence intensity of Zn-HKUST-1 quenches completely in the presence of 200 ppm of 1,3-dinitrobenzene and also this figure shows the sensitivity of Zn-HKUST-1 toward 100 ppm of 1,3-dinitrobenzene is more than the sensitivity of this framework toward 200 ppm of nitrobenzene. This results explicit sensitivity

of Zn-HKUST-1 towards nitroaromatics is significantly enhanced by increasing the NO_2 group, which facilitates the analyte-framework interaction probably by the formation of π-π stacking and C-H••π interactions.
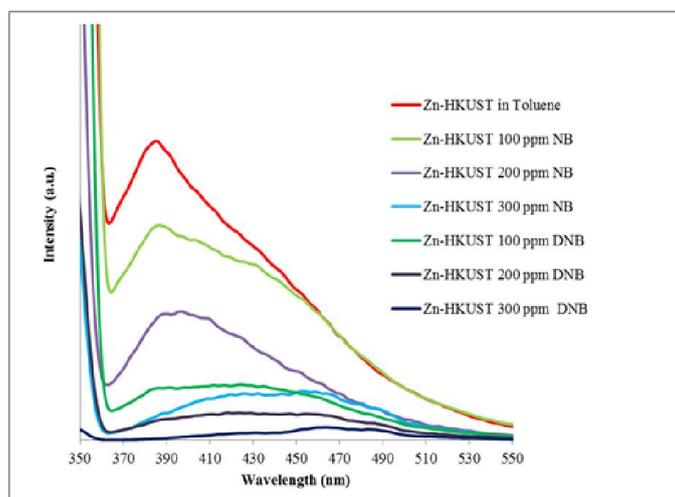

Figure 5. Comparison of fluorescence emission spectra of Zn-HKUST-1 in the presence of different concentrations of nitrobenzene and 1,3-dinitrobenzene.

Trinitrotoluene (TNT) or more specifically 2,4,6-trinitrotoluene, is a chemical compound with the formula $C_6H_2(NO_2)_3CH_3$. This yellow-colored solid is sometimes used as a reagent in chemical synthesis, but it is best known as an explosive material with convenient handling properties. The explosive yield of TNT is considered to be the standard measure of bombs and other explosives. In chemistry, TNT is used to generate charge transfer salts. While the two words are sometimes used interchangeably in common conversation, TNT is not the same as dynamite, a special formatting of nitroglycerin for use as an industrial explosive [24].TNT is still widely used by the United States military, as well as construction companies around the world. The majority of TNT currently used by the US military is manufactured by Radford Army Ammunition Plant near Radford, Virginia [25].

Due to this introduction about TNT, the importance of sensing that by Zn-HKUST-1 sensor is more highlighted. Therefore the sensing ability of Zn-HKUST-1 towards NACs, namely nitrobenzene, 1,3-dinitrobenzene and 2,4,6-trinitrotoluene (TNT) has been evaluated.Comparison offluorescence emission spectra of Zn-HKUST-1 in the presence of 100 ppm nitrobenzene, 1,3-dinitrobenzene and TNT is shown in figure 6a.The result reveal that the fluorescence quenching efficiency follows the order of nitrobenzene <1,3-dinitrobenzene <TNT, and explicit that the Zn-HKUST-1 sensor is

significantly more sensitive towards TNT than other two analyst.The quenching percent's of fluorescence intensity in the presence of 100 ppm of nitrobenzene, 1,3-dinitrobenzene and TNT were achieved 35%, 50% and 79.5% respectively, (Figure6b). The results again showed that Zn-HKUST-1 metal-organic framework can be effective in detecting explosives such as TNT.
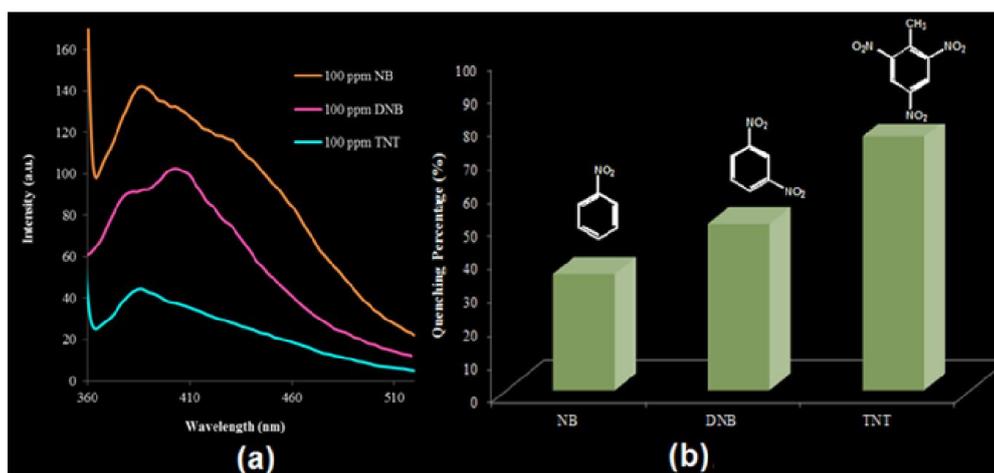

Figure 6. (a) Comparison of fluorescence emission spectra of Zn-HKUST-1 in the presence of 100 ppm nitrobenzene, 1,3-dinitrobenzene and TNT, (b) Comparison of quenching percent of Zn-HKUST-1 fluorescence in the presence of 100 ppm nitrobenzene, 1,3-dinitrobenzene and TNT.

Another part of the work nano-structure synthesis of Zn-HKUST-1 framework using ultrasound (sonochemical) was examined. Nanoplates of the MOF were obtained in DMF by ultrasonic irradiation, while single crystals of the framework were prepared by a conventional heating method.FT-IR spectra of the products obtained by the sonochemical method and of the bulk material are indistinguishable (Figure7).
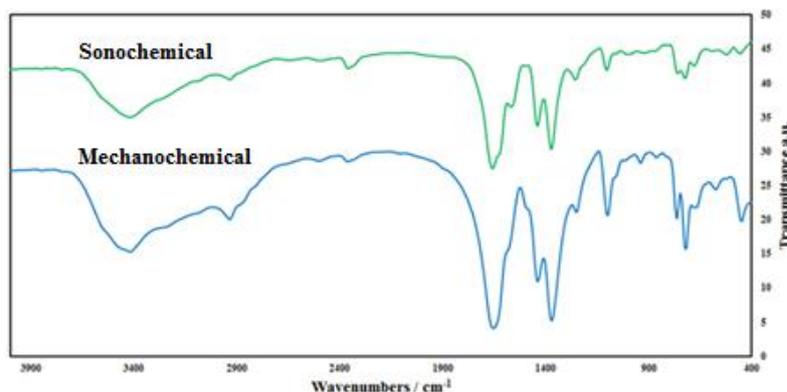
Figure7. Comparison between FT-IR spectraof mechanical-synthesized (down) and nanostructure of Zn-HKUST-1 prepared by sonochemical process (up).

Figure 2a shows the simulated XRD pattern from single crystal X-ray data of Zn-HKUST-1 (1) in comparison with the XRD pattern of the single crystal MOF as synthesized (2) and a typical sample of the framework prepared by the sonochemical process (3). All the diffraction peaks can be well-indexed to a known bulk phase of Zn-HKUST-1, and acceptable matches, with slight differences in 2θ, were observed between the simulated and experimental powder X-ray diffraction patterns.The significant broadening of thepeaks indicates that the particles are of nanometer dimensions.

The morphology and size of Zn-HKUST-1 prepared by the sonochemical method were characterized by field emission scanning electron microscopy (FE-SEM). In order to investigate the role of concentration of initial reagents [26], reactionswere performedwith three different concentrationsof initial reagents (0.01, 0.02 and 0.04 mol L^{-1}) by sonicator power 12 W.Figure 8a shows the FE-SEM of the nanoparticles of Zn-HKUST-1 prepared in concentration of initial reagents 0.02 mol L^{-1} that have plate-like morphology. Comparison between the samples with different concentrations shows that high concentrations (0.04 mol $L^{-1)}$ of initial reagents increased size of particles and agglomeration (Figure 8c).Whileparticles sizes produced using lower concentrations of initial reagents (0.01 mol L^{-1},Figure8b) are moreuniform and smaller than those produced using higher concentration. Interestingly, reduce in concentration of initial reagentsup to 0.01 mol L^{-1} ultimate to micro-rod structures; actually the particles have mixture of plate and rod-likemorphologies.
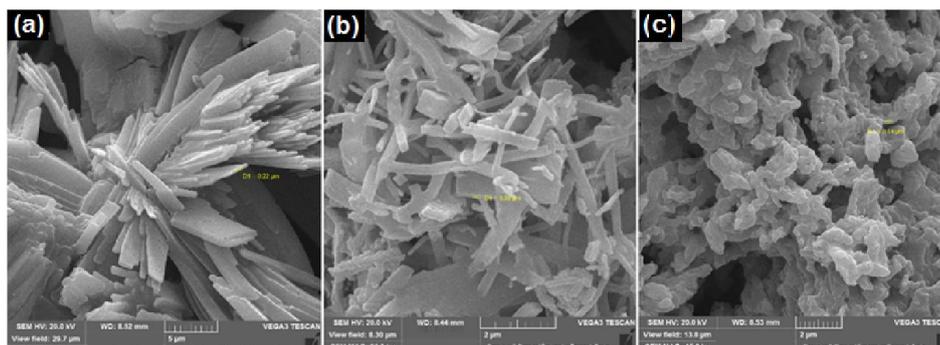
Figure 8. FE-SEM images of Zn-HKUST-1 nanoparticles prepared by sonochemicalmethod under ultrasonic power of 12 W in concentration of initial reagents (a) 0.02, (b) 0.01 and (c) 0.04 mol L^{-1}.

Accordingly, in order to find the effect of ultrasonic power on morphology and size of nanostructured Zn-HKUST-1 framework, the synthesis was also performed at different ultrasonic power (18 W) for two concentrations of initial reagents (0.02 and 0.01 mol L^{-1}). As shown in figure9a increase in the ultrasonic power from 12 to 18 W, leads to smaller particle size and morphology of nano-structures with a mixture of rod and plate-like. Figure9b shows how plate's thickness decreases with the increase in the ultrasonic power from 12 to 18 W. Furthermore, the nanoplates of Zn-HKUST-1 framework, has been synthesized at ultrasonic power 18 W.
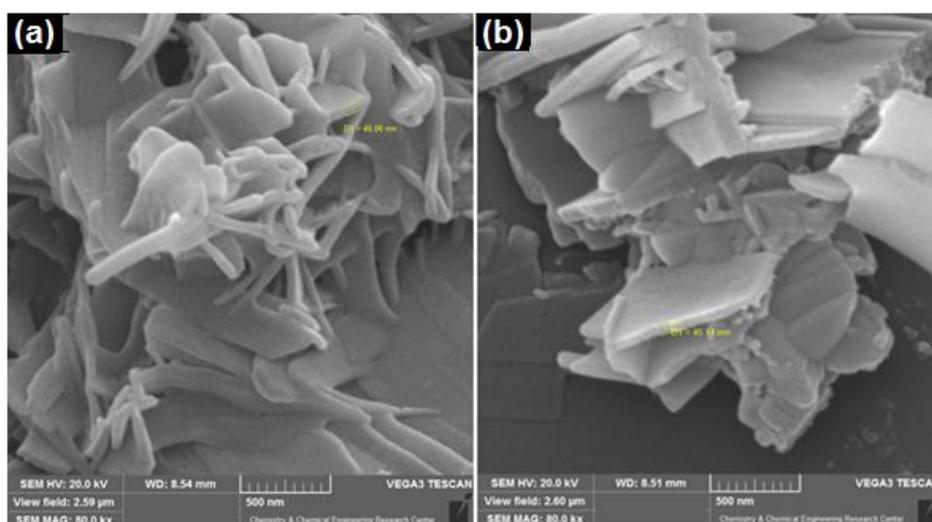

Figure 9. FE-SEM images of Zn-HKUST-1 nanoparticles prepared by sonochemical method under ultrasonic power of 18 W in concentration of initial reagents (a) 0.01 and (b) 0.02 mol L^{-1}.

Conclusion

In this work, Zn-HKUST-1 metal-organicframework was synthesizedby fast and also environmentally friendly physical mixing (mechanochemical) method. To identify products spectroscopy methods such as FT-IR and PXRD were employed. Also, the synthesis of Zn-HKUST-1 by the sonochemical method provides us an opportunity to investigate the self-assembly of these complexes in the nano-domain. After measuring and comparing the fluorescence emission intensity of this metal-organic framework by is suspended in aromatic solvents such as toluene, benzene and nitrobenzene, its sensing ability to detect explosive- like NACs such as nitrobenzene, 1,3-Dinitrobenzene and TNT was tested. The results showed that the sensitivity of Zn-HKUST-1 to TNT is more than two other analytes. The percent of fluorescence quenching of Zn-HKUST-1 in the presence 100 ppm of these analyst obtained 35%, 50% and 79/5% for nitrobenzene,1,3-Dinitrobenzene and TNT respectively. This has been reflected in its different potentials for sensing organic aromatic molecules and implies that this MOFcould be a potential sensor for organic analytes.

References

[1]S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita,S. Kitagawa,*J. Am. Chem. Soc,*129, 2607(2007).

[2] L. R. MacGillivray, Metal-organic frameworks: design and application. Wiley: Hoboken, N.J, (2010).

[3] H-C. Zhou, J. R. Long, O. M. Yaghi, *Chem. Rev.,*112, 673(2012).

[4]T. R. Cook, Y. R. Zheng, P. J. Stang, *Chem. Rev.*, 113, 734(2012).

[5]L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.*, 112, 1105(2011).

[6] Chen, B. Xiang, S.G. Qian, *Acc. Chem. Res.,*43, 1115(2010).

[7] S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee, S. K. Ghosh, *Angew. Chem. Int. Ed.*, 52, 2881(2013).

[8] S. Abedi, A. Morsali, *New J. Chem.,*39, 5108 (2015).

[9] S. Pramanik, C. Zheng, X. Zhang, T. J. Emge, J. Li, *J. Am. Chem. Soc.*, 133, 4153 (2011).

[10]L. Wang, Y. A. Li, F. Yang, Q. K. Liu, J. P. Ma, Y. B. Dong, *Inorg. Chem.*, 53, 9087 (2014).

[11] Y. S. Xue, Y. He, L. Zhou, F. J. Chen, Y. H. B. Xu, X. Z. You, B. Chen, *J. Mater. Chem. A*, 1, 4525 (2013).

[12] H. Hu, S. Liu, C. Chen, J. Wang, Y. Zou, L. Lin, S. Yao, *Analyst*, 139, 5818 (2014).

[13] J. A. Greathouse, N. W. Ockwig, L. J. Criscenti, T. R. Guilinger, P. Pohl, M. D. Allendorf, *Phys. Chem. Chem. Phys.,* 12, 12621(2010).

[14]C. S. Hawes, Y. Nolvachai, C. Kulsing, G. P. Knowles, A. L. Chaffee, p. J. S. R. Marriott, D. R.Turner, *Chem. Commun.*, 50, 3735 (2014).

[15] N. Stock, S. Biswas, *Chem. Rev.*,112, 933 (2012).

[16] À. Ruyra, A.Yazdi, J. Espín, A. Carné-Sánchez, N. Roher, J. Lorenzo, I. Imaz,D. Maspoch, *Chem. Eur. J.*,21, 2508(2015).

[17] H. Guo,Y. Zhu,S. Wang,S. Su,L. Zhou,H. Zhang,*Chem. Mater.*, 24, 444 (2012).

[18]A. Carne,I. Imaz,K. C.Stylianou,D. Maspoch,*Chem. Eur. J.*, 20, 5192 (2014).

[19] R. Sabouni, H. Kazemian, S. Rohani,*Chem. Eng.J.*, 165, 966(2010).

[20]V. Safarifard, A. Morsali, S.W. Joo, *Ultrason. Sonochem.*, 20, 1254 (2013).

[21] K. S. Suslick, *J. Acoust. Soc. Am.*, 89, 1885(1991).

[22] D.W. Jung, D.A. Yang, J. Kim, W.S. Ahn, *Dalton Trans*, 39, 2883 (2010).

[23]G. M. Sheldrick, SADABS; University of Gottingen: Gottingen, Germany(1996).

[24]G. I. Brown, The Big Bang: a History of Explosives. Sutton Publishing. ISBN 0-7509-1878-0. 151 (1998).

[25]T. Urbanski, Chemistry and Technology of Explosives. 1. Pergamon Press. ISBN 0-08-010238-7. 389 (1964).

[26] K. Liu, H. You, G. Jia, Y. Zheng, Y. Huang, Y. Song, M. Yang, L. Zhang, H. Zhang, *Cryst. Growth Des.*, 10, 790(2009).