Accepted Manuscript

Ultrasound-assisted synthesis and characterization of new metal-organic framework based on azobenzene-4,4-dicarboxylic acid: Precursor for the fabrication of Co_3O_4 nano-particles

Fatemeh Parsa, Massomeh Ghorbanloo, Mohammad Yaser Masoomi, Ali Morsali, Peter C. Junk, Jun Wang

PII:	S1350-4177(18)30476-0
DOI:	https://doi.org/10.1016/j.ultsonch.2018.03.014
Reference:	ULTSON 4127
To appear in:	Ultrasonics Sonochemistry
Received Date:	2 December 2017
Revised Date:	4 March 2018
Accepted Date:	24 March 2018



Please cite this article as: F. Parsa, M. Ghorbanloo, M.Y. Masoomi, A. Morsali, P.C. Junk, J. Wang, Ultrasoundassisted synthesis and characterization of new metal-organic framework based on azobenzene-4,4-dicarboxylic acid: Precursor for the fabrication of Co₃O₄ nano-particles, *Ultrasonics Sonochemistry* (2018), doi: https://doi.org/ 10.1016/j.ultsonch.2018.03.014

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Ultrasound-assisted synthesis and characterization of new metalorganic framework based on azobenzene-4,4-dicarboxylic acid: Precursor for the fabrication of Co₃O₄ nano-particles

Fatemeh Parsa,^a Massomeh Ghorbanloo,^a Mohammad Yaser Masoomi,^b Ali Morsali,^{*b} Peter C. Junk^c, Jun Wang^c

^a Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran

^b Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-

175, Tehran, Iran. E-mail: Morsali_a@modares.ac.ir

^c College of Science & Engineering, James Cook University, Townsville Queensland, 4811, Australia NAT

ABSTRACT

Azobenzene groups are widely known as photochromic ligands thus particularly interesting building block for designing receptors for neutral or charged guests. A new metal-organic framework, $[Co_3(adc)_3(DMF)_4]$.2DMF (compound 1) (adc = azobenzene-4,4-dicarboxylic acid, DMF = N,N-dimethylformamide), was synthesized by solvothermal methods and structurally characterized using X-ray crystallography and a range of spectroscopic techniques. Also, nanorods of compound **1** have been synthesized by a sonochemical process and characterized by field emission scanning electron microscopy (FE-SEM) and powder X-ray diffraction (PXRD). The effect of sonication time and concentration of the initial reagents on the size and morphology of the MOF have been optimized. Results indicate that decreasing of initial concentration and increasing ultrasound radiation time lead to small size nanorods of compound **1**. Thus, ultrasound radiation affects the size of nanorods. After heat treatment, the cobalt ionbased metal organic framework nanorods can be converted into porous Co3O4 nanoparticle.

Keywords: Metal-organic framework; Sonochemical; Ultrasound; Nano-structure; Single crystal X-ray diffraction.

1. INTRODUCTION

Metal–organic frameworks (MOFs) are known as porous materials which have attracted great attention due to their potential applications in gas storage [1, 2], separation [3, 4], ion exchange [5], sensing [6, 7], catalysis [8, 9], and drug delivery [10]. An interesting feature of MOFs over other porous materials is the ability to tune their channel size, topology and functionality by deliberate design [11]. Flexible design is one of the essential properties of these materials that can be employed by choosing suitable organic ligands and inorganic secondary building units (SBUs) [12, 13].

Material growth control at the scale of sub-micrometer is of great importance in the field of nanotechnology. Additionally, reducing the size of MOFs to the micro- and nanoscale has been quite attractive [14-17]. Various parameters such as molar ratio of reactants, solvent, reaction time, pH, pressure and etc affect the size and morphology of pre-designed supramolecular assemblies. Nowadays a variety of synthetic strategies have been employed by various research groups in supramolecular synthesis including microwave-assisted heating, electrochemical synthesis, mechanochemistry and ultrasound irradiation that result in different yields, reaction time, particle size, morphology and final products [18, 19]. Among these synthetic strategies, ultrasound synthesis is one of the nontraditional techniques, facile, fast, and environmentally friendly and energy efficient method with advantages in operation under ambient conditions and lowered reaction times [20].

In recent years there have been many efforts to design functionalized MOFs with photochromic sites. The introduction of H2azdc in the formation of CPs and MOFs has resulted in limited

success. Azobenzene and its derivatives are widely known as photochromic ligands which could sustain clean and efficient invertible photoisomerization for the azo bond between cis and trans states under irradiation or heating, as well as other conditions [21].

MOFs are useful precursors for the preparation of inorganic nano-materials such as metal oxides via calcination at high temperature in the air [22, 23]. The chemical and physical properties of solid materials mostly depend on the size and shape of the materials which the compounds are made especially in the case of nano-materials [24-26]. In recent years, Co_3O_4 as a magnetic p-type semi-conductor has attracted great attention due to interesting properties such as excellent cycle reversibility and high specific capacity [27,28].

Herein, we report the simple preparation of micro and nano structures of an azine-functionalized MOF by two solvothermal and sonochemical methods. The effects of sonication time and initial concentration of reagents on shape and size of the nanostructures have been investigated. Moreover, similar to other solid-phase fabrication approaches, metal–organic frameworks can be easily transformed into metal oxides via simple calcination at high temperature in the air. To proceed, we report Co_3O_4 nano-structures synthesized by direct calcination of the single crystals and nano-sized compound **1** at 550 °C.

2. EXPERIMENTAL

Materials and Physical Techniques

All reagents for the syntheses and analysis were commercially available and used as received. The infrared spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500-4000 cm⁻¹ using the KBr disk technique. A single crystal of compound **1** was selected and mounted on a loop in inert oil and transferred to the cold gas stream of the diffractometer on the MX1 Beamline at the Australian Synchrotron. The data were corrected for

absorption and beam corrections based on the multiscan technique as implemented in *SADABS*. The structures were solved by conventional methods and refined by full-matrix least-squares on all F^2 data using SHELX-2014 in conjunction with the Olex2 graphical user interface. Melting points were measured on an Electrothermal 9100 apparatus. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu-K α radiation. The molecular structure scheme and simulated XRD powder pattern based on single crystal data were prepared using Mercury software. The sonicator used in this study was a Misonix Sonicator 3000 with an adjustable power output (maximum 600 W at 50/60 kHz). A horn type tube Pyrex reactor was custom-made and fitted to the sonicator bar. The samples were also characterized by field emission scanning electron microscope (FE-SEM) TESCAN MIRA with a gold coating.

Synthesis of azobenzene-4,4-dicarboxylic acid (adcH₂) ligand

4-nitrobenzoic acid (2.0 g, 12 mmol) and NaOH (5.75 g, 144 mmol) were dissolved in 30 mL of water. As 20 mL of glucose (13.0 g, 72 mmol) aqueous solution was added at 70 0 C, a yellow precipitate formed which was vigorously stirred and upon further addition of glucose a brown solution resulted. The mixture was heated to reflux under a stream of air overnight. The light brown precipitate was dissolved in 10 mL of water, and acetic acid was used to adjust the pH of the solution in the range of 5 to 6. The light pink precipitate was filtered and washed several times with distilled water and dried in vacuum to give azobenzene-4,4-dicarboxylic acid (Scheme 1). Yield: 60%. 1H NMR (500 MHz, DMSO-d₆) d (ppm): 8.3 (d, 4H, J = 8.4 Hz), 8.15 (d, 4H, J = 8.4 Hz).



Scheme 1. Schematic representation of the production of adcH₂ ligand.

Synthesis of single crystals of [Co₃(adc)₃(DMF)₄].2DMF

To isolate single crystals of $[Co_3(adc)_3(DMF)_4].2DMF$, azobenzene-4,4-dicarboxylic acid (0.27 g, 1mmol), $Co(NO_3)_2.6H_2O$ (0.3g, 1 mmol) and DMF (15 ml) were placed in a Teflon-lined stainless steel autoclave under autogenous pressure and heated at 100 °C for 3 days. The mixture was then gradually cooled to room temperature over 48 hours. Red crystals formed on the walls of the container with a 61% yield m.p. > 300 °C. FT-IR data (KBr pellet, cm⁻¹): selected bands are: 682(m), 786(m), 1112(m), 1388(m), 1615(s), 1658(vs), 2923(br) and 3409(br).

Synthesis of [Co₃(adc)₃(DMF)₄].2DMF nano-structure by a sonochemical process

To prepare nano-sized compound **1**, 15 ml solution of Cobalt(II) acetate tetrahydrate and azobenzene-4,4-dicarboxylic acid (1:1) in DMF (Table 1) were positioned in a high-density ultrasonic probe, operating with a maximum power output of 12 W. The obtained precipitate was filtered off, washed with DMF and then dried in air, m.p. > 300 °C. IR bands are 682(m), 786(m), 1112(m), 1388(m), 1615(s), 1658(vs), 2923(br) and 3409(br).

The morphology and size of nanostructures mostly depend on various parameters such as the concentration of starting reagents, ultrasonic irradiation time and power. For investigation, the effect of starting material concentration on size and morphology of compound **1**, the synthesis processes were carried out with different concentrations (0.1M, 0.05M, 0.02M, and 0.0125M). Moreover, for studying the role of ultrasonic irradiation time on size and morphology of compound **1** the process with the initial reagents concentration of 0.1 M has been done in two different ultrasonic times (table 1).

Synthesis of Co₃O₄ nanostructures

To prepare Co_3O_4 nano-particles, samples of compound **1** were calcined at 550 ^{0}C for 5 h. After cooling, a brown precipitate was obtained. SEM images of these materials show the formation of Co_3O_4 nanoparticle in the range of 70–120 nm.

Sample name	Concentration (M)	Time	power	Morphology
	[adc]/[Co(OAc)2]			
Sample A	[0.1]/[0.1]	60min	12W	non-uniform rod
Sample B	[0.1]/[0.1]	3:30h	12W	non-uniform rod
Sample C	[0.05]/[0.05]	3:30h	12W	uniform rod
Sample D	[0.02]/[0.02]	3:30h	12W	uniform rod
Sample E	[0.0125]/[0.0125]	3:30h	12W	uniform rod

Table 1: Experimental	details for synthesis	of nano compound 1.
-----------------------	-----------------------	---------------------

3. RESULTS AND DISCUSSION

Single crystals of compound **1** were obtained by mixing azobenzene-4,4-dicarboxylic acid and $Co(NO_3)_2.6H_2O$, in DMF at 100 °C. The FT-IR spectrum of compound **1** shows the symmetric $v_{sym}(COO)$ and asymmetric $v_{as}(COO)$ vibrations of the carboxylate groups at 1409 cm⁻¹ and 1604 cm⁻¹, respectively for both crystals and ultrasonic synthesized compound **1**. Also the characteristic absorption peak ($v_{C=O} = 1659$ cm⁻¹) of DMF is observed in the IR spectrum (Fig.



Fig. 1. FT-IR spectra of simulated and ultrasound compound 1

X-ray crystallography reveals that $[Co_3(adc)_3(DMF)_4].2DMF$ (compound 1) crystallizes in the monoclinic space group $P2_1/n$ (Table 2). There are two different Co(II) centers in the asymmetric unit of 1 in which Co1 is octahedrally coordinated by six oxygen atoms (CoO₆) of six different adc ligands, while Co2 has distorted octahedral geometry interacting with four oxygen atoms of three adc ligands and two oxygen atoms from coordinated DMF molecules. Two of the adc

ligands adopt μ_2 ligation and the other coordinates as a chelating $\kappa^2 O$ ligand and extends the structure in three dimensions (Fig. 2). The supramolecular features in this complex are guided and controlled by weak directional intermolecular interactions. The chains interact with each other through p–p stacking interactions creating a 3D supramolecular framework. Compound **1** shows limited porosity with the calculated void space per unit cell for guest-free framework of 31.6% (1205.8 Å³). The topological analysis of Compound 1 exhibits a uninodal 6-connected hxl/Shubnikov plane net (3,6) with {3⁶ .4⁶ .5³ } topology. Also compound **1** is nonporous toward N2 at 77 K and 1 bar.



Fig. 2 (a) SBU of compound **1** showing coordination environment about Co1 and Co2. (b) Representation of the three-dimensional structure of compound **1**. The hydrogen atoms were omitted for clarity.

Thermogravimetric analysis of compound **1** synthesized by the ultrasound technique shows that the trapped guest DMF molecules are released from the network upon heating to about 200°C, which causes 16% weight loss of the material corresponding to two DMF molecules (calculated 16.5%). The second gradual weight loss appears between 200-380 °C (~5%), the third sharp







For studying the effect of sonication time as a parameter on size and morphology of nanostructured compound **1**, the synthesis process was performed at a constant concentration of initial

reagents of 0.1 M but at two different sonication times. At 60 min and 3:30 h, aggregated nanoparticles were obtained, and at the longer reaction time, the particles were smaller than the shorter reaction time (Fig. 4). For monitoring the role of the concentration of initial reagents on size and morphology of compound **1** the process at the optimized time of 3:30 h has been done in three different concentration of starting material (0.05M, 0.02M, 0.0125M). The results indicate that the higher concentration of reagents causes increasing particle size. Lower concentrations of initial reagents reduce the size of particles and lead to a uniform distribution of particle size (Fig.

5).



Fig. 4: SEM images of compound 1 synthesized by the sonochemical method at two different reaction times, (a) sample A and (b) sample B. In both cases the initial concentration of reagents were [0.1] M.



Fig. 5. SEM images of compound 1 synthesized by the sonochemical method at different concentration of starting material (a) sample C, (b) sample D and (c) sample E. In all three cases the reaction time was 3:30 h.

A comparison between powder X-ray diffraction (PXRD) patterns of the simulated (derived from the single crystal structure of **1** and experimental (resulting from the sonochemical process) shows a good match between these two PXRD patterns indicating that the sonochemically synthesized **1** is structurally identical to that prepared through solvothermal reaction



Fig. 6: PXRD patterns of simulated and ultrasound of compound 1

Furthermore, the sonochemically synthesized nanorods of compound **1** were used as a precursor for the preparation of MOF-derived Co_3O_4 nano-structures. Calcination of the nano-sized compound **1** has been done at 550 °C in a static atmosphere of air for 5 h. Fig. 7 shows the XRD pattern of the Co_3O_4 nanoparticles. These nanoparticles have shown the good crystallinity because of the existence of sharp peaks in the XRD pattern. The Bragg diffraction peaks in the range of $2\theta = 20-80$ indicate the typical cubic spinel structure with the lattice parameters of a =8.0837 Å and Z = 8 and S.G = Fd3m which are in JCPDS card file No. 42-1467. An SEM image of the residue obtained from the direct calcination of compound **1** shows the formation of Co_3O_4 nano particles in the range of 70-120 nm (Fig. 9).



Fig. 7. PXRD patterns of Co₃O₄ form of compound 1



Fig.8. SEM images of compound 1 synthesized by the solvothermal



Fig.9. SEM images of Co₃O₄ nanoparticles

4. Conclusion

A new Co(II) based metal–organic framework, $[Co_3(adc)_3(DMF)_4]$.2DMF has been readily and quickly synthesized by the solvothermal and sonochemical process. Compound **1** was characterized using different spectroscopic techniques and X-ray crystallography. Ultrasonie method for preparation of the MOFs has some advantages such as: needing shorter reaction times, production of MOFs with better yields and also at nano-sizes. Morphology and sizes of the nano-structures depend on the concentrations of initial reagents and the reaction time. The results show that a lower concentration of reagents leads to decrease in particle size. Also, increasing of reaction time leads to nano-structures with rod-like morphology and decreases the particle size of the nano-structures. We believe that it would be of interest to pursue such studies to clarify the design of MOFs with favorite morphology, size distribution and shape. Nano-structures of Co₃O₄ were produced by calcination of compound **1** at 550 ⁰C for 5 h.

Acknowledgment

Support of this investigation by Tarbiat Modares University is gratefully acknowledged. Appendix A. Supplementary data

The supplementary crystallographic data was deposited with the Cambridge Crystallographic Data Centre (CCDC) as entry CCDC 1588088.

	CCDC Identification code	1588088	
	Empirical formula	$C_{66}H_{74}Co_3N_{14}O_{20}$	
	Formula weight	1560.18	
	Temperature	100.15 K	
	Wavelength	0.71073 Å	
	Crystal system	monoclinic	
	Space group	P2 ₁ /n	2
	Unit cell dimensions	a = 14.765(3) Å	
		b = 17.325(4) Å	
		c = 16.395(3) Å	
		α = 90.00°	
		$\beta = 114.59(3)^{\circ}$	
		$\gamma = 90.00^{\circ}$	
	Cell volume, Å ³	3813.6(16)	
	Z value	2	
	Density (calc.) (g.cm ⁻³)	1.359	
	Absorption coefficient	0.722 mm ⁻¹	
	F(000)	1618	
	Crystal size	$0.11\times0.05\times0.02\ mm^3$	
	θ range for data collection	1.95 to 24.99°	
	Index ranges	-17≤h≤17	
	0	-20≤k≤20	
		-19≤1≤19	
	Reflections collected/unique	34707/6683 [R(int) = 0.0457]	
C 1	Data/restraints/parameters	6683/106/419	
	Goodness-of-fit on F ²	1.075	
	Final R indices (I>2.00 σ (I))	R1 = 0.0955, wR2 = 0.2462	
	R indices (all data)	R1 = 0.0997, wR2 = 0.2501	
	Largest diff. Peak, hole	2.180 and -1.071 e.Å ⁻³	

 $\hat{\boldsymbol{c}}$

Table 2. Crystal data and structure refinement of $[Co_3(adc)_3(DMF)_4] \cdot 2DMF(1)$.

References:

[1] M.Y. Masoomi, K.C. Stylianou, A. Morsali, P. Retailleau, D. Maspoch, Selective CO2 capture in metal–organic frameworks with azine-functionalized pores generated by mechanosynthesis, Crystal Growth & Design, 14 (2014) 2092-2096.

[2] V. Safarifard, S. Rodríguez-Hermida, V. Guillerm, I. Imaz, M. Bigdeli, A.A. Tehrani, J. Juanhuix, A. Morsali, M.E. Casco, J. Silvestre-Albero, Influence of the Amide Groups in the CO2/N2 Selectivity of a Series of Isoreticular, Interpenetrated Metal–Organic Frameworks, Crystal Growth & Design, 16 (2016) 6016-6023.

[3] T.H. Bae, J.S. Lee, W. Qiu, W.J. Koros, C.W. Jones, S. Nair, A High-Performance Gas-Separation Membrane Containing Submicrometer-Sized Metal–Organic Framework Crystals, Angewandte Chemie International Edition, 49 (2010) 9863-9866.

[4] B. Chen, C. Liang, J. Yang, D.S. Contreras, Y.L. Clancy, E.B. Lobkovsky, O.M. Yaghi, S. Dai, A Microporous Metal–Organic Framework for Gas-Chromatographic Separation of Alkanes, Angewandte Chemie, 118 (2006) 1418-1421.

[5] T.K. Prasad, D.H. Hong, M.P. Suh, High Gas Sorption and Metal-Ion Exchange of Microporous Metal–Organic Frameworks with Incorporated Imide Groups, Chemistry–A European Journal, 16 (2010) 14043-14050.

[6] M. Bagheri, M.Y. Masoomi, A. Morsali, Highly sensitive and selective ratiometric fluorescent metal–organic framework sensor to nitroaniline in presence of nitroaromatic compounds and VOCs, Sens. Actuators, B, 243 (2017) 353-360.

[7] M. Bagheri, M.Y. Masoomi, A. Morsali, A. Schoedel, Two Dimensional Host–Guest Metal– Organic Framework Sensor with High Selectivity and Sensitivity to Picric Acid, ACS Applied Materials & Interfaces, 8 (2016) 21472-21479.

[8] A.A. Tehrani, S. Abedi, A. Morsali, J. Wang, P.C. Junk, Urea-containing metal-organic frameworks as heterogeneous organocatalysts, Journal of Materials Chemistry A, 3 (2015) 20408-20415.

[9] M.Y. Masoomi, S. Beheshti, A. Morsali, Shape control of Zn (II) metal–organic frameworks by modulation synthesis and their morphology-dependent catalytic performance, Crystal Growth & Design, 15 (2015) 2533-2538.

[10] P. Horcajada, C. Serre, G. Maurin, N.A. Ramsahye, F. Balas, M. Vallet-Regi, M. Sebban, F. Taulelle, G. Férey, Flexible porous metal-organic frameworks for a controlled drug delivery, Journal of the American Chemical Society, 130 (2008) 6774-6780.

[11] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'keeffe, O.M. Yaghi, Hydrogen storage in microporous metal-organic frameworks, Science, 300 (2003) 1127-1129.

[12] T.R. Cook, Y.-R. Zheng, P.J. Stang, Metal–organic frameworks and self-assembled supramolecular coordination complexes: comparing and contrasting the design, synthesis, and functionality of metal–organic materials, Chemical reviews, 113 (2012) 734-777.

[13] O.K. Farha, J.T. Hupp, Rational design, synthesis, purification, and activation of metalorganic framework materials, Accounts of chemical research, 43 (2010) 1166-1175.

[14] T. Uemura, S. Kitagawa, Nanocrystals of coordination polymers, Chemistry letters, 34 (2005) 132-137.

[15] M.Y. Masoomi, A. Morsali, Morphological study and potential applications of nano metalorganic coordination polymers, RSC Adv., 3 (2013) 19191-19218.

[16] M.Y. Masoomi, M. Bagheri, A. Morsali, Porosity and dye adsorption enhancement by ultrasonic synthesized Cd(II) based metal-organic framework, Ultrason. Sonochem., 37 (2017) 244-250.

[17] M.Y. Masoomi, A. Morsali, P.C. Junk, J. Wang, Ultrasonic assisted synthesis of two new coordination polymers and their applications as precursors for preparation of nano-materials, Ultrason. Sonochem., 34 (2017) 984-992.

[18] J.H. Bang, K.S. Suslick, Applications of ultrasound to the synthesis of nanostructured materials, Advanced materials, 22 (2010) 1039-1059.

[19] W.-J. Son, J. Kim, J. Kim, W.-S. Ahn, Sonochemical synthesis of MOF-5, Chemical Communications, (2008) 6336-6338.

[20] M. Montazerozohori, A. Masoudiasl, S. Farokhiyani, S. Joohari, P. McArdle, Sonochemical synthesis of a new cobalt (II) complex: Crystal structure, thermal behavior, Hirshfeld surface analysis and its usage as precursor for preparation of CoO/Co 3 O 4 nanoparticles, Ultrasonics sonochemistry, 38 (2017) 134-144.

[21] G.S. Kumar, D. Neckers, Photochemistry of azobenzene-containing polymers, Chemical Reviews, 89 (1989) 1915-1925.

[22] M.Y. Masoomi, A. Morsali, Applications of metal–organic coordination polymers as precursors for preparation of nano-materials, Coordination Chemistry Reviews, 256 (2012) 2921-2943.

[23] M.Y. Masoomi, A. Morsali, Sonochemical synthesis of nanoplates of two Cd(II) based metal–organic frameworks and their applications as precursors for preparation of nano-materials, Ultrason. Sonochem., 28 (2016) 240-249.

[24] S.A.A. Razavi, M.Y. Masoomi, A. Morsali, Stimuli-Responsive Metal–Organic Framework (MOF) with Chemo-Switchable Properties for Colorimetric Detection of CHCl3, Chem. Eur. J., 23 (2017) 12559-12564.

[25] M. Bagheri, M.Y. Masoomi, A. Morsali, High organic sulfur removal performance of a cobalt based metal-organic framework, J. Hazard. Mater., 331 (2017) 142-149.

[26] M.Y. Masoomi, M. Bagheri, A. Morsali, P.C. Junk, High photodegradation efficiency of phenol by mixed-metal-organic frameworks, Inorg Chem Front, 3 (2016) 944-951.

[27] T. Maruyama, S. Arai, Electrochromic properties of cobalt oxide thin films prepared by chemical vapor deposition, Journal of the Electrochemical Society, 143 (1996) 1383-1386.
[28] L.M. Al-Qirby, S. Radiman, C.W. Siong, A.M. Ali, Sonochemical synthesis and characterization of Co3O4 nanocrystals in the presence of the ionic liquid [EMIM][BF4], Ultrasonics sonochemistry, 38 (2017) 640-651.

Highlights

- Synthesis of a new Co(II) based metal-organic framework.
- Effects of sonication time and initial concentration of reagents on shape and size of nanostructures have been investigated.
- High concentrations of initial reagents increased particles size of compound 1.
- Low concentrations of initial reagents leaded to nanostructures.
- Preparation of Co3O4 nanoparticles by thermolysis of metal-organic framework.