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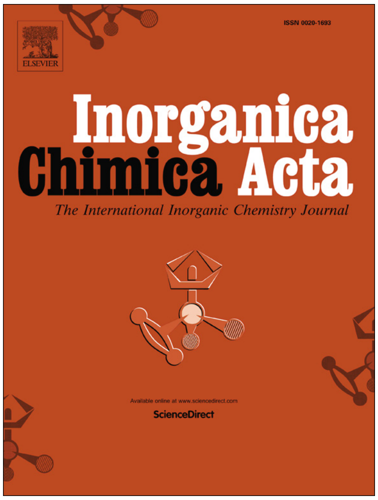

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Ultrasound and Solvothermal Syntheses of a New Urea-based Metal-Organic Framework as a Precursor for Fabrication of Cadmium(II) Oxide Nanostructures

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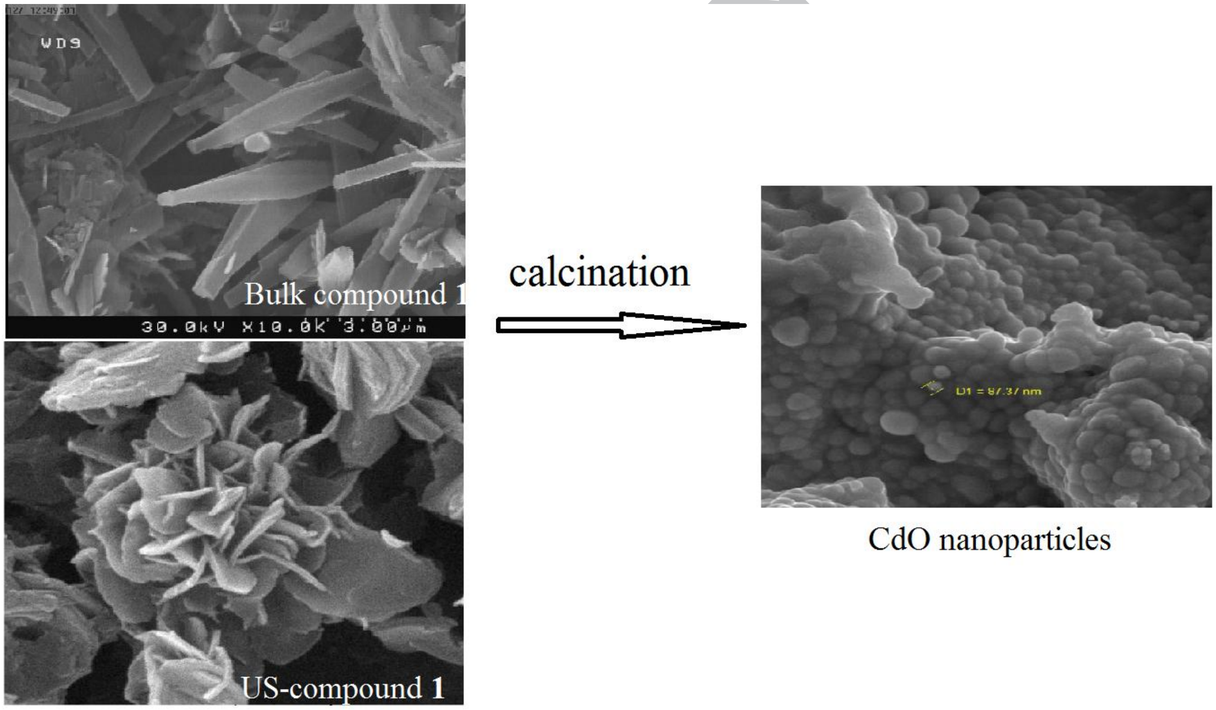

Abstract

Dramatic advances in nanostructured MOFs have been strongly promoted by the introduction and development of new synthetic methods that control the size, morphology, and nano/microstructure. High intensity ultrasound method suggests an environmentally friendly, facile and versatile synthetic method to these nanostructured materials that are complicated to synthesize by commonly used methods. Both Solvothermal and sonochemical methods were used to synthetize the new urea-based metal-organic framework $[Cd(L1)(DMF)_3]$ (**1**). Compound **1** was structurally characterized by using X-ray crystallography and spectroscopically by different techniques. The effect of concentration of the initial reagents, time of sonication and sonication power on size and morphology has been studied. The results indicate that decreasing concentration of initial reagents, along with increasing ultrasounic radiation time, cause a dramatic effect on the size and morphology of compound **1**. Calcination of the nano-sized plate-like particles of compound **1** at 550 °C under air atmosphere yields CdO nanoparticles.

Keywords: Metal-organic framework, Sonochemical, Nano-structure, hydrogen bonding, urea group

1. Introduction

Metal-organic frameworks are ideal candidates for applications such as gas storage [1-3], separation [4], sensing [5, 6], and catalysis [7] due to their tunable nature, defined reaction environments and permanent porosity [8]. Taking advantage of this features, chemists have focused on design and synthesize novel MOFs having particularly desired and predetermined functions and properties. Designability of these materials can be determined by choosing suitable organic linkers and inorganic secondary building units (SBUs) [9]. Urea group is well-known for self-aggregation and self-quenching behavior, resulting in loss of activity. Urea based Metal-organic frameworks are a new class of interesting heterogeneous materials that can form strong H-bond which make them exciting candidates for investigation of host-guest interactions [10-12]. The interesting idea of incorporating this hydrogen bond donating group into a metal-organic framework backbone was initially proposed by Farha, Hupp, Scheidt, and coworkers [13, 14]. They investigated the catalytic reactions of the urea-containing frameworks carried out by these HBD (Hydrogen Bond Donating) catalysts. Urea derivatives have been shown to greatly accelerate key bond-forming transformations relative to earlier HBD catalysis or sensors. Although this improved acidity is a promising advancement in HBD derivatives, the strong hydrogen-bonding nature of the urea-based strut also drives self-association. Immobilization of the urea functionality would be the ideal method to prevent both recycling and self-quenching issues (Figure1). There are several different synthetic approaches that have been offered for the preparation of metal–organic frameworks. A typical strategy for the synthesis of MOF structures involves conventional electric (CE) heating, in which metal and organic components are directly reacted under specific synthetic conditions in order to obtain oriented growth [15]. Conventional methods suffer from the long times of reactions, usually several days for solvothermal, and several weeks for diffusion methods. Moreover, the reaction building blocks of framework under solvothermal conditions has to be conducted out at highly elevated temperatures (373-523 K) and pressures (1-10MPa). On the other hand, controlling the growth of materials at the sub-micrometer scale is of essential importance in the field of nanotechnology. It is interesting to use the ultrasonic irradiation in the preparation of nano or microstructures of MOFs. Ultrasonic assisted synthesis involves shorter reaction time, milder reaction condition and offers enhanced control of particle size and morphology compared to conventional electric (CE) heating, furthermore, it can be considered as a green synthetic method [16, 17]. Compared to micro-sized materials, the ratio of surface area to volume is extremely increased in nano materials and quantum mechanical effects, such as the ‘‘quantum size effect’’, began to play an important role [18, 19]. The application of ultrasound (US) for MOFs synthesis is now positioned as one of the most powerful tools in MOFs and CPs synthetic process. Jhung and Khan have recently reviewed the synthesis of MOFs by the application of MW and US irradiation. They compared these two non-traditional methods with each other as well as with conventional electric (CE) heating method to figure out which techniques were faster and result in smaller nanoparticles. The advantage of US and MW over CE heating was clarified in terms of the degree of acceleration on the reaction’s rate, the selective synthesis of some MOF structures and the reduction in size of MOF crystals. Application of MOFs as templates can lead to the facile preparation of different desired nano-materials. Considering suitable MOF precursors with special morphologies, under standard experimental conditions, the desired morphologies can be obtained. Nano MOFs precursors can be used to synthesize nano-materials with more desired properties. Based on the conditions, MOFs precursor may be applied for the preparation of nano sized materials including metals, metal oxides, metal sulfides and other useful nano-materials. Metal oxides show attractive electronic, optical, photoelectronic, thermo electronic, and bactericidal properties. It is clear that various properties can be observed depending on the nature of metal ions. In recent years, cadmium(II) oxide (CdO), an n-type semiconductor with a well-established direct band gap of 2.5 eV, has been studied intensely for its different applications. Some of which are in photovoltaic (PV) solar cells, gas sensors, photodiodes, transparent electrodes, and sensors. The nanoparticles of CdO play a dominant role in the further improvement of its optical and electrical properties [20-22]. For these reasons, there have been some efforts for the preparation of cadmium oxide nanostructures with various synthetic methods such as solvothermal, micro-emulsion, sol–gel synthesis, precipitation, etc. Thermal decomposition of MOFs is an alternative mean to prepare metal oxide nanostructures with different sizes and morphologies [23-26].

In this work, we report the synthesis of compound **1**, $[Cd(L1)(DMF)_3]$, as urea-functionalized MOF by the solvothermal and sonochemical methods. The combination of a urea-functionalized ligand, 4,4'-(carbonylbis(azanediyl))dibenzoic acid and an appropriate metal ion could produce materials that avoid the possibility of self-quenching while possessing spatially distinct hydrogen-bonding sites. In addition effects of sonication time, sonication power and initial concentration of reagents on shape and size of nanostructures have been investigated. Results indicate that using a higher concentration of starting materials led to larger particle sizes. Also increasing the reaction time together with ultrasonic power decreased the size of nano-structures of compound **1**. Moreover, metal-organic frameworks can be transformed into metal oxides via calcination procedure at high temperature in air, which is a useful method to synthesize metal oxides with controlled morphology, structure, particle size and properties

[27]. In order to examine this approach, the nanoparticles of CdO were synthesized by calcination of sonochemically synthesized compound **1** nanoparticles at 550°C in air atmosphere.

2. Experimental Section

2.1.Materials and Physical Techniques

All starting reagents, including Cd(II) nitrate tetrahydrate, Cd(II) acetate dihydrate, 1,1'-Carbonyldiimidazole and 4-Aminobenzoic acid were purchased from Aldrich and Merck Company and used as received. Ultrasonic generation was carried out in an ultrasonic bath SONICA-2200 EP (frequency of 40 KHz). Melting points were measured on an Electrothermal 9100 apparatus. The samples were characterized by field emission scanning electron microscope (FE-SEM) SIGMA ZEISS and TESCAN MIRA with gold coating. IR spectra were recorded using Thermo Nicolet IR 100 FT-IR. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu-Kα radiation. X-ray data were collected on a Bruker Apex II diffractometer using MoKα radiation. The structures were solved using direct methods and refined using a full-matrix least squares procedure based on F^2 using all data. Hydrogen atoms were placed at geometrically estimated positions. Details relating to the crystal and the structural refinement are presented in Table 1. Full details of crystal data and structure refinement, in CIF format, are available as Supplementary Information. CCDC 1565307.

2.2.Synthesis

The ligand 4,4'-(carbonylbis(azanediyl))dibenzoic acid (L1) was synthesized according to the reported procedure. [5]

2.2.1 Synthesis of compound 1 as single crystals

A mixture of 0.308 g of $Cd(NO_3)\cdot4H_2O$ (1 mmol), and 0.3 g of ligand L1 (1 mmol) was dissolved in 20 mL of DMF. The mixture was then placed in a Teflon reactor and heated at 100 °C for 72 h producing **1** as white crystals with yields of 40%. FT-IR data (KBr pellet, cm^{-1}), selected bands: 3408 (w), 2907 (w), 1667 (vs), 1599 (s), 1521 (s), 1371 (m), 1310 (w), 1173 (m), 1018 (w), 843 (w), 782 (w), 536 (w).

2.2.2. Synthesis of compound 1 as nanoparticles

A mixture of 0.266 g of $Cd(CH_3COO)_2\cdot2H_2O$ (1 mmol), 0.3 g of ligand L1 (1 mmol) in 20 mL of DMF was reacted in an ultrasonic bath at ambient temperature and atmospheric pressure for different time and concentrations of metal and ligand. The resulting white powder was isolated by centrifugation, washed with DMF three times and dried at 80˚C. Yield: 68%. FT-IR data (KBr pellet, cm^{-1}), selected bands: 3407 (w), 2903 (w), 1666 (vs), 1598 (s), 1523 (s), 1374 (m), 1311 (w), 1172 (m), 1016 (w), 845 (w), 782 (w), 536 (w).

2.2.3. Synthesis of CdO nanoparticles

To prepare cadmium(II) oxide nanoparticles compound **1**, prepared under ultrasound condition, was calcined at 550 ˚C for 5 h. After gradual cooling of samples, white precipitates of CdO particles were obtained. For all calcined samples, CdO nanoparticles were characterized as a final product. SEM images of these CdO nanoparticles show a size distribution in the range of 60–160 nm.

Results and Discussion

Hydrogen-bonding donating compound has emerged as a promising biomimetic alternative to Lewis acid materials. Urea, thiourea and squaramide moieties are the best common hydrogen-bond donors compound. However, their significant tendency to undergo self-aggregation often decreases their solubility and reactivity. Recently, scientists have found a promising way around this problem by immobilizing the hydrogen-bonding donating strut on metal–organic frameworks (Figure1). compound **1** was synthesized by combining Cd(NO$_3$)·4H$_2$O and L1 ligand using the solvothermal method at 100 °C for 72 h to give suitable X-ray quality crystals. X-ray crystallography indicates that compound **1** crystallizes in the monoclinic $P2_1/c$ space group. The asymmetric unit consists of one Cd(II) ion, one L1 ligand, and three DMF molecules. Cd ion has a distorted pentagonal bypyramidal environment and is coordinated to four oxygen atoms of carboxylate groups [Cd-O distances in the range: 2.3923(17)-2.3502(16) Å] from two symmetry equivalent L1 ligands and three oxygen atoms of DMF molecules [Cd-O distances in the range: 2.3321(18)-2.304(2) Å] generating linear chains -L1-Cd-L1-Cd- running along two directions [1,1,0] and [1,-1,0]. The ligand L1 bridge by chelation of the two carboxylic groups (κ^1*O*,*O*’) on two Cd^{2+} ions, so that, four oxygen atoms from two different ligands occupy four equatorial positions around each metal center. The remainder equatorial and the two axial positions of the pentagonal pyramidal coordination environments of Cd(II) are occupied by the three DMF molecules. The resulting chain motifs are quite linear showing a Cd…Cd distance, through the L1 ligand, of 17.94 Å. Along the chains the phenyl rings belonging to the same L1 molecule are twisted by a dihedral angle of 31.4°, while the carbonyl group of the urea fragment along the chains are all oriented in the same direction. A view of the crystal structure of **1** showing the coordination environment about Cd atom is reported in Figure 2. Structural analysis reveals that the urea N-H groups of L1 ligands are involved in inter-chain hydrogen bonds with two carboxylic oxygen atoms of two L1 ligands [N…O 2.815(3) , 2.821(3) Å] resulting in supramolecular 3-coordinated layers of topology 8^2.10-KIa that pack along [0,0,1] as ABAB (Figure 3). The carbonyl group of the urea moiety in L1 is not involved in H-bonds. The thick layer KIa is one of the most frequently observed 3-coordinated layers after **hcb** [29].

Figure 4 illustrates the TGA curve of the compound **1** synthesized by solvothermal technique. The results show a residual solvent loss between 100- 210 ˚C (~3% weight loss) and two subsequent distinguished weight losses. The first sharp weight loss occurs between 211-300 ºC (ca. 42%) and the second gentle slope of weight loss appears between 300-500 ºC. Compound **1** is thermally stable up to 211 °C, as evidenced by the fact that no additional weight loss was observed at those temperatures, after which the framework eventually decompose.

Figure 5 illustrates the FT-IR spectra of compound **1** samples synthesized using the two different synthetic methods. The spectra acquired on samples prepared by ultrasound and conventional methods show the characteristic bands of the dicarboxylate groups of the L1 ligands for the asymmetric and symmetric vibrations at 1599, 1373 cm^{-1} and 1598, 1374 cm^{-1}, respectively (Figure 5). Such evidences confirm the same coordination modes of the carboxylate groups for samples prepared by the two methods. The absence of the expected characteristic bands at 1710-1680 cm^{-1} for the protonated carboxylate groups in both compounds indicates the complete deprotonation of 4,4'-(carbonylbis(azanediyl))dibenzoic acid (L1) in the reaction with Cd(II) salt. Both of these spectra show the asymmetric vibration of urea groups around 1715 cm^{-1}. Also, the characteristic FT-IR peak of DMF is presented at 1667 cm^{-1}. Figure 6 shows PXRD patterns of as-synthesized samples prepared by solvothermal and sonochemical methods. The good match between these two PXRD patterns indicate that the sonochemically synthesized sample is structurally identical to that prepared by the solvothermal method. Short crystallization time in addition to accelerated nucleation in sonochemical synthesis, accompanied by low temperature and ambient pressure of the reaction, make homogeneous smaller particles. These features would be useful and applicable for commercially fabricating pellets or membranes used in an adsorption/separation process. Crystals made by the US-assisted process have similar or even superior porosity properties compared to those synthesized from the traditional methods, though the synthesis is much faster. All the frameworks synthesized at room temperature could be seemingly synthesized via US, and there are only a few reports demonstrating that some of the MOFs could not be obtained under ambient conditions without application of any US irradiation. Usually, US method cannot produce crystals of suitable size for the single crystal X-ray analysis. The morphology and size of nanostructures prepared using ultrasonic technique are dependent on various parameters such as the concentration of initial reagents, ultrasonic reaction time and irradiation power. For studying the effect of starting materials concentrations on size and morphology of compound **1**, the synthesis processes were done with different concentrations (0.01, 0.005 and 0.001M). Moreover, in order to investigate the role of power ultrasonic irradiation on size and morphology of compound **1** the process with the initial reagents concentration of 0.001 M has been done at three different ultrasonic power (6, 12 and 18 W). Also for monitoring the role of ultrasonic time on size and morphology of nano-plate the synthesis has been done at three different ultrasonic irradiation time.

The SEM micrographs of bulk synthesized compound **1** are shown in Figure 7. The BFDH analysis was performed to compare the observed morphology obtained under solvotermal synthesis to that predicted from molecular arrangements in the crystal structure. Acceptable matches were observed between the predicted BFDH morphology and the SEM images. BFDH analyses estimate the faces that are likely to appear in the external morphology. In order to investigate the role of ultrasound irradiation in syntheses of compound **1** nano-structures and the effect of ultrasonic equipment, Tecna ultrasonic bath has been used for the preparation of compound **1**. The morphology and size of prepared compound **1** were investigated by field emission scanning electron microscopy (FE-SEM) through changing three parameters: sonication power, sonication time and concentration of initial materials, Table 2. Almost in all cases, nano-plate was the dominant morphology. To investigate the role of concentration of starting materials on the nature of products, reactions were performed in three different concentrations of initial reagents: [Cd] = [L1] of [0.01], [0.005] and [0.001]. The FE-SEM micrographs of compound **1** indicate plate morphology with diameters ranging from nano to micro dimensions. As shown in Figure 8 comparison between these samples reveals that high concentrations of starting materials [0.01], tend to yield larger particles (range of 80–160 nm), while, using lower concentrations of initial reagents produced smaller particles [0.005] and [0.001] (range of 40–120 nm). All these results were achieved at the sonication power of 12 W. The size of the crystals can be influenced by a number of factors, like the solubility of the sample in the chosen solvent, the number of nucleation sites and time. These results show that there exists a clear influence of the initial concentration on the nucleation rate. A decrease of this rate results in a lower number of nuclei formed, leading to the formation of larger crystals and it happens when we use high concentration of initial reagent. To investigate the effect of ultrasound irradiation power on morphology and size of compound **1**, the reaction was performed under three different ultrasonic powers: 12W, 18W and 24W. SEM images demonstrated that using high power ultrasound irradiation (24 W) leads to uniform nanosized plate-like morphology when compared to lower powers (12W). As a result, higher power ultrasound irradiation generated nanostructures with a smaller size (Figure 9). Accordingly, to explore the effect of sonication time, the synthesis was also performed at two different reaction times (Figure 8). Comparison between the samples with different ultrasonic irradiation times shows that higher irradiation time decreased plate’s size and increased the homogenization of particle size distribution.

Cadmium oxide used as a transparent conductive material prepared as a transparent conducting film back. CdO particles undergo band gap excitation when exposed to UV-A light and is also selective in phenol photo degradation. With this background of multifunctionality CdO, it was thought worthwhile to use the nano-sized MOF as an organic-inorganic precursor in the CdO preparation. Therefore, the sonochemically synthesized nanoplates of compound **1** were used as a precursor for the preparation of MOF-derived CdO nanospheres. Figure 6 indicates the PXRD pattern of the residue obtained from calcination of compound **1** at 550 ºC under air atmosphere for 5 h. The Bragg diffraction peaks in the range of 2Ө = 20–80° indicate the typical patterns of the cubic monteponite structure of CdO (JCPDS No. 05-0640, a = 4.69 Å). SEM image of the residue obtained from the direct calcination of sonochemically prepared compound **1** at 550 °C shows the formation of CdO particles in the range of 60–160 nm Figure 10.

3. Conclusion

In summary, a new metal-organic framework, based on 4,4'-(carbonylbis(azanediyl))dibenzoic acid ligand (L1), was synthesized by using solvothermal and sonochemical methods. The effects of various parameters such as different irradiation time, various concentrations of starting reagents and different irradiation power were also examined to obtain homogenous nano-structures. Appropriate nano-sized particles of compound **1** were obtained at lower concentrations of starting materials and higher ultrasound irradiation power. Particle sizes of the nanoparticles depend on the concentration and reaction conditions. Moreover, calcination of compound **1** at different sizes produced nanoparticles of CdO.

Acknowledgment

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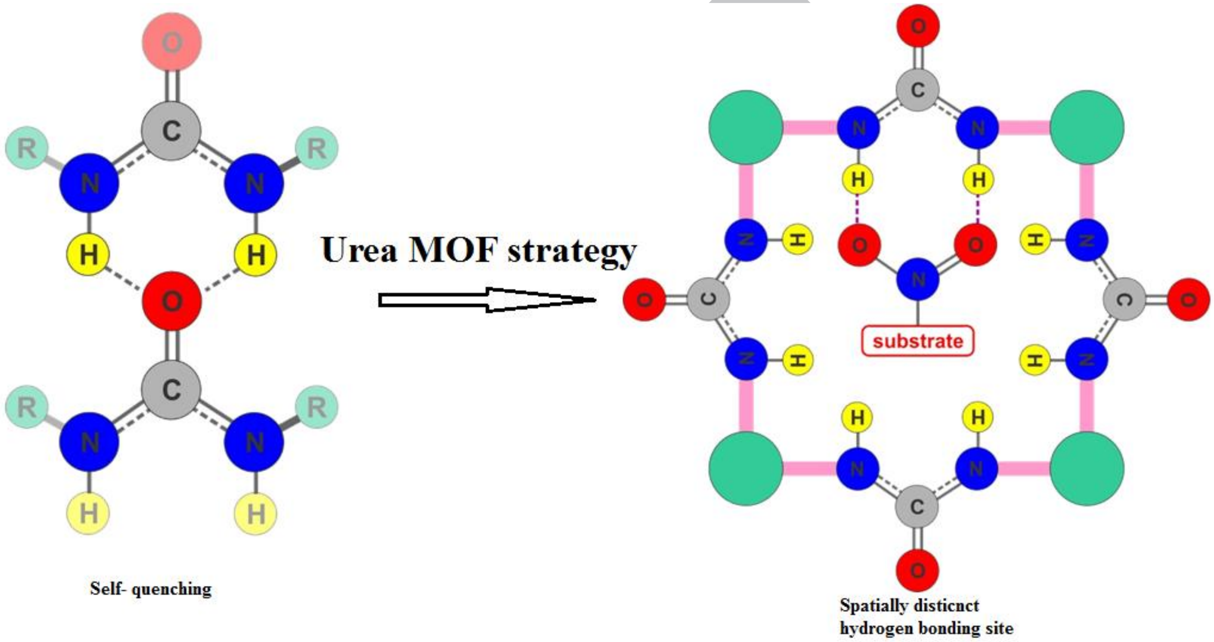

Figure1: Idealized self-association pattern of urea derivatives and Idealized structure of urea functionalized compound **1** MOF.

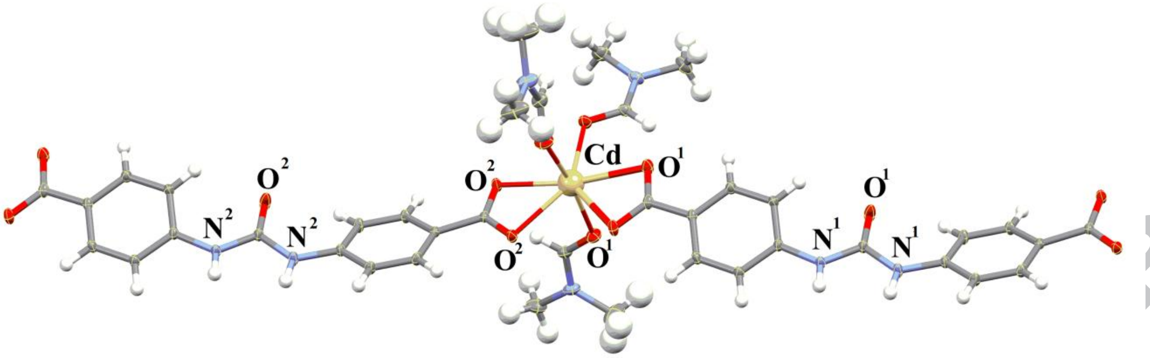

Figure 2: A portion of the structure of compound **1**, showing the coordination geometry around the cadmium ion. (1) at x, y, z and (2) at -1+x, -1+y, z

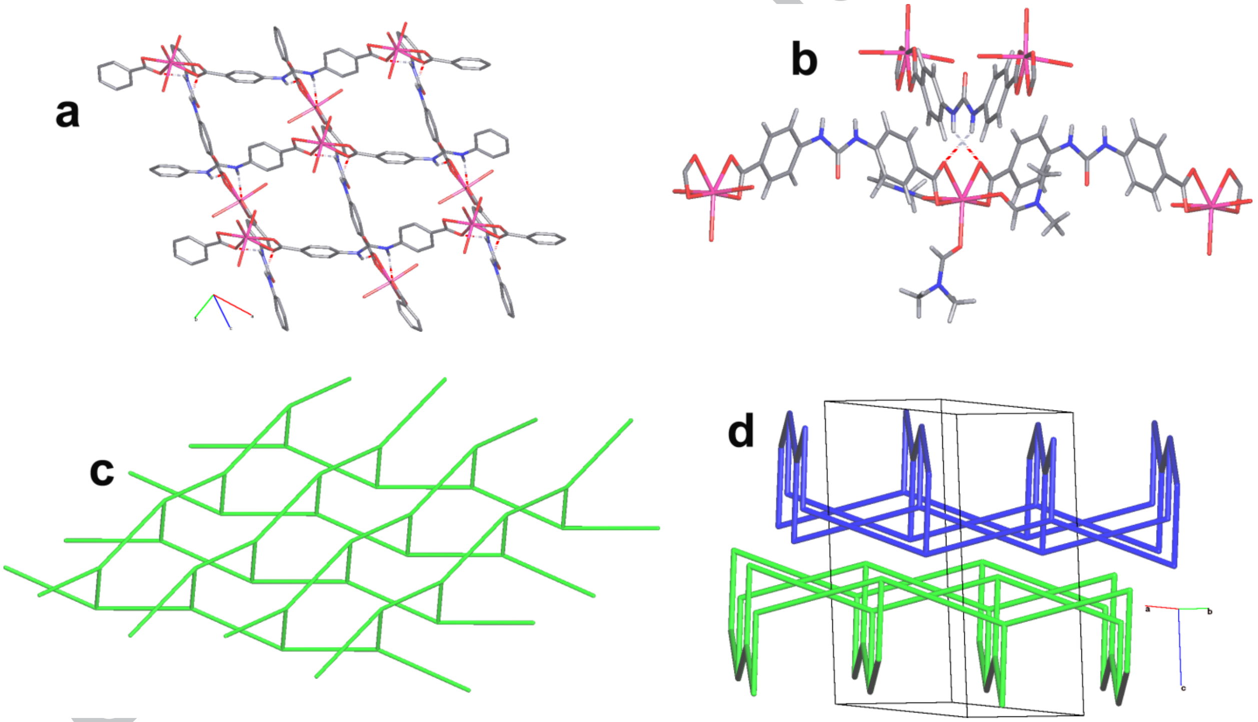

Figure 3: Representations of the three-dimensional structure of compound **1**. a) The supramolecular layer built through N-H…O hydrogen bonds between adjacent chains. b) View of the hydrogen bond pattern. c) A simplified 8^2.10-KIa layer. d) A view of the ABAB packing of the layers.

Table 1. Structural data and refinement parameters for compound **1**.

formula	$C_{24}H_{31}CdN_5O_8$
fw	629.94
λ/Å	0.71073
T/K	150(2)
crystal system	Monoclinic
space group	$P2_1/c$
a/Å	15.3360(11)
b/Å	9.3010(7)
c/Å	19.9600(14)
β/°	95.8350(10)
V/Å^3	2832.3(4)
D_{calc}/Mg.m^{-3}	1.477
Z	4
μ (mm^{-1})	0.824
F(000)	1288
2θ (˚)	50.00
R (int)	0.0381
GOOF	1.070
R_1^a(I>2σ(I))	0.0372
wR_2^b(I>2σ(I))	0.0873
.	

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)2]^{½}$.

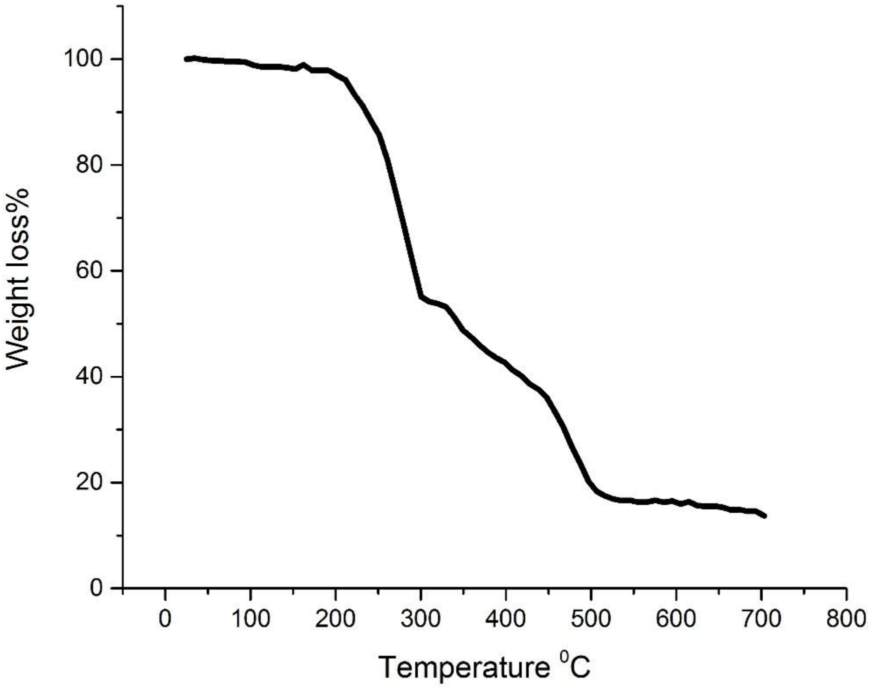

Figure 4: Thermogravimetric analysis of compound **1**

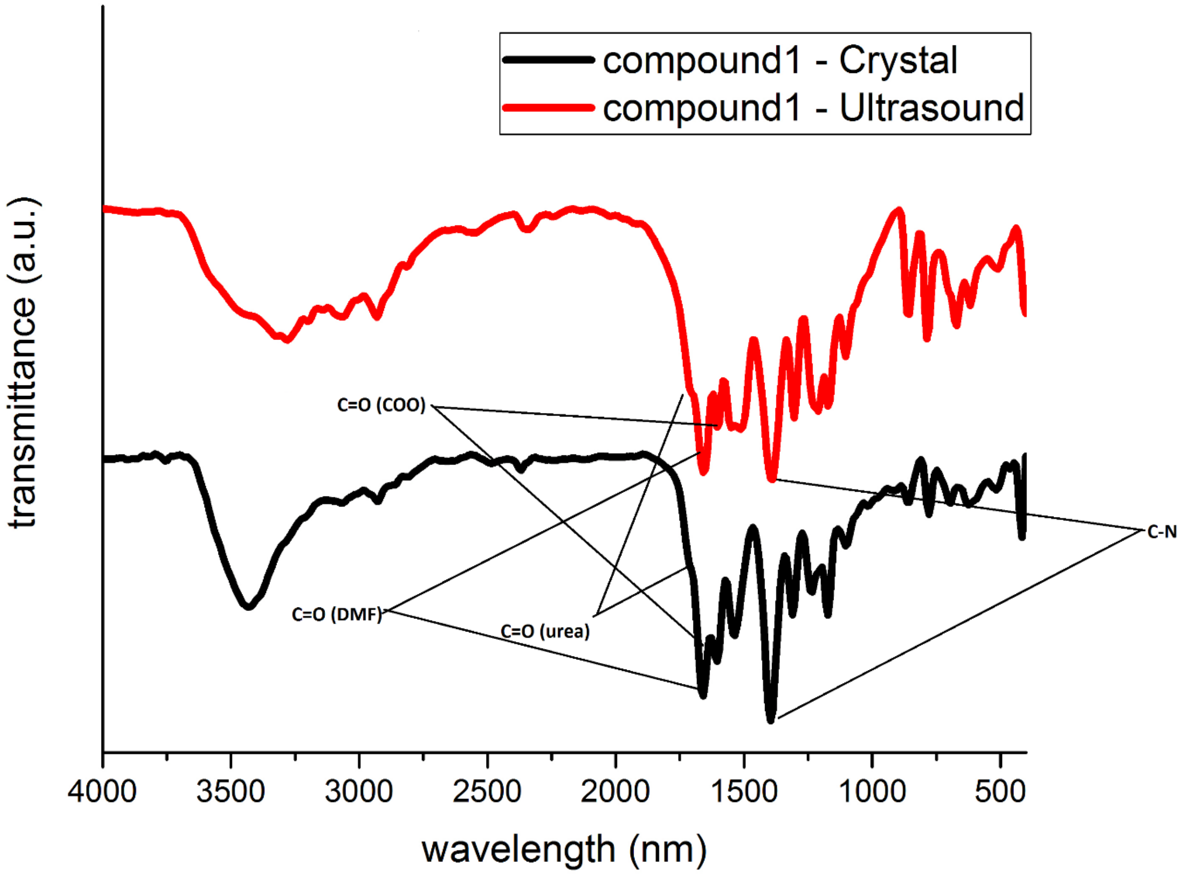

Figure 5: IR spectra of crystals and nano-plates of compound **1** produced by conventional heating (black) and sonochemical method (red), respectively.

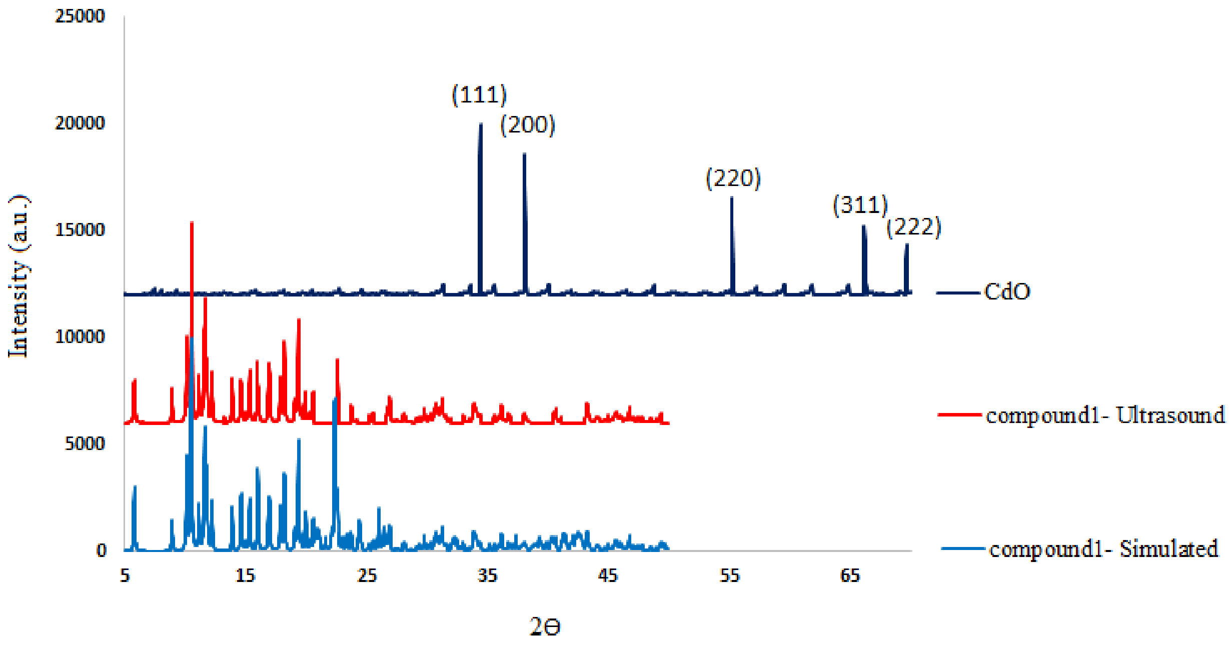

Figure 6: PXRD patterns of simulated (orange) and ultrasound prepared (blue) compound **1** and of CdO (grey) obtained by its calcination.

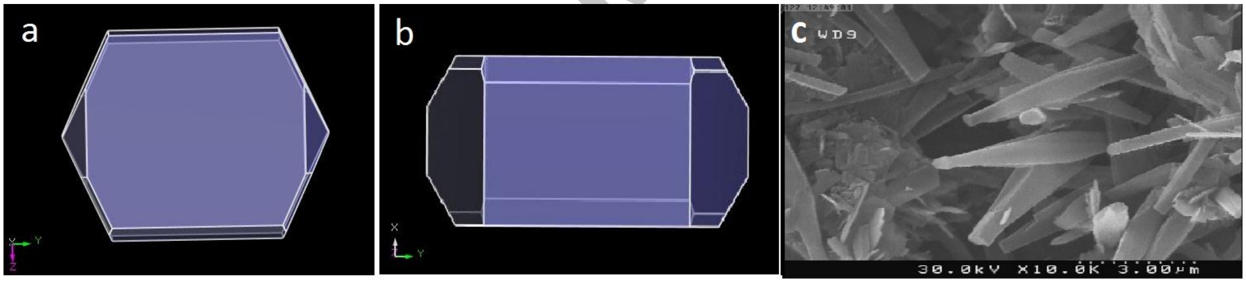

Figure 7: Predicted morphology of compound **1** in DMF (a, b) by BFDH method and FE-SEM images of bulk compound **1** in DMF (c)

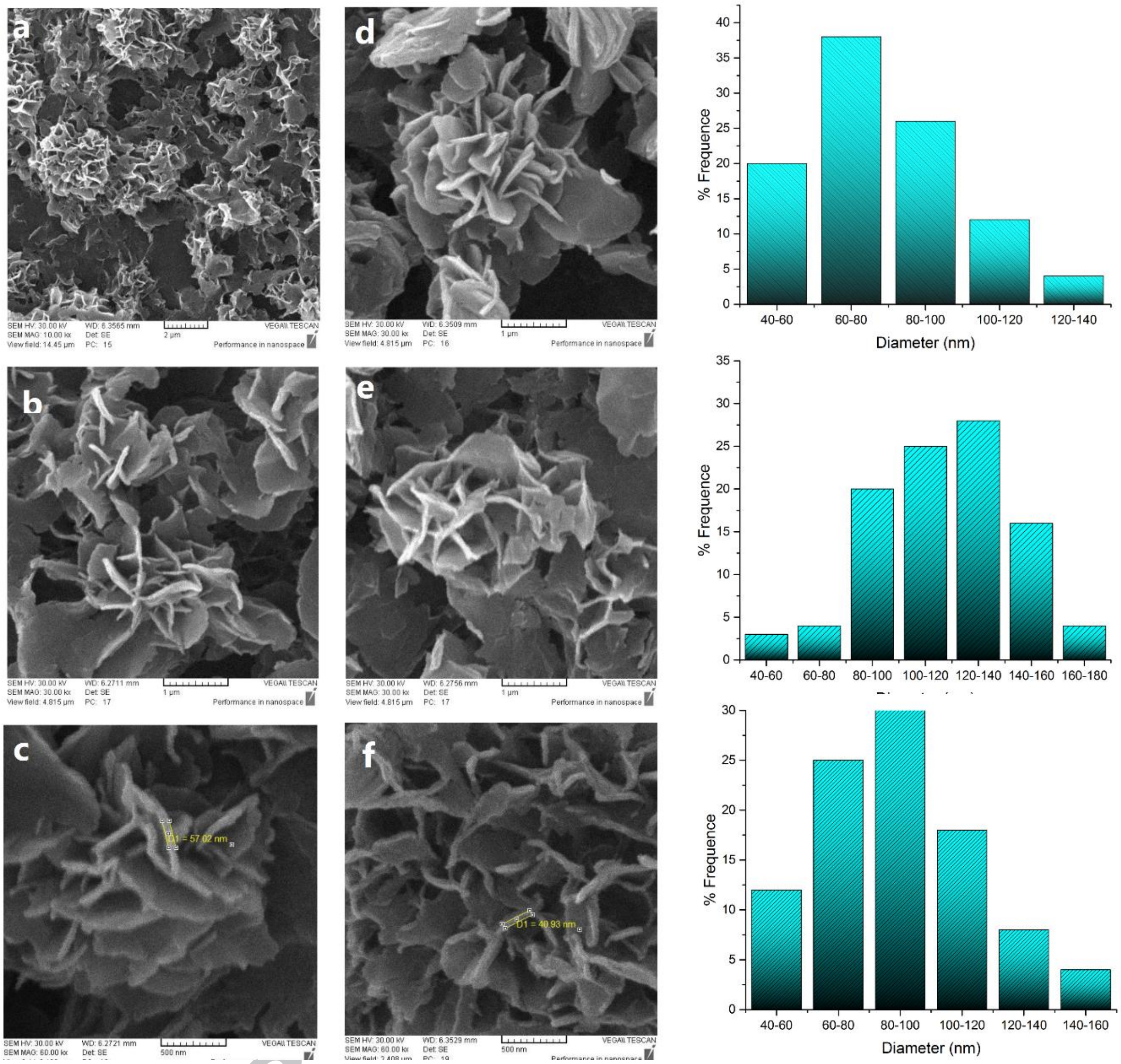

Figure 8: SEM images of compound **1** synthesized by sonochemical method : Concentration $[L_1]/[Cd(OAc)_2]$ and Time a) [0.01]/[0.01]; 15min b) [0.005]/[0.005]; 15min c) [0.001]/[0.001]; 15min d) [0.01]/[0.01]; 30min e) [0.005]/[0.005]; 30min f) [0.001]/[0.001]; 30min

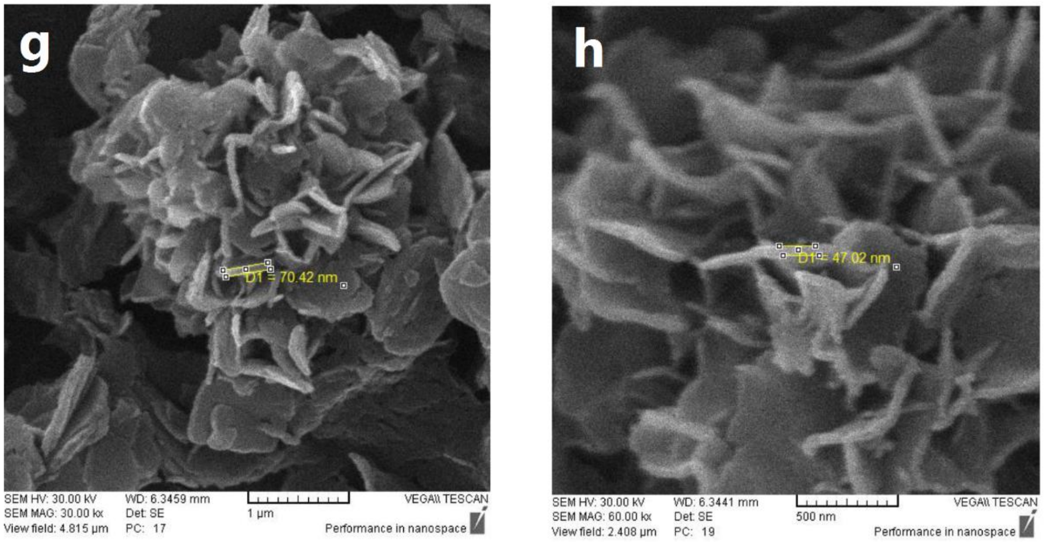

Figure 9: SEM images of compound **1** synthesized by sonochemical method: Concentration $[L_1]/[Cd(OAc)_2]$,Time [0.001]/[0.001]; 30min and g) sonication power 18w h) 24h

Table 2: Experimental details for the synthesis of compound **1** as nanoparticles under different sonochemical conditions.

Sample name	Concentration $[L_1]/[Cd(OAc)_2]$	Time	power
Compound 1-a	[0.01]/[0.01]	15min	12W
Compound 1-b	[0.005]/[0.005]	15min	12W
Compound 1-c	[0.001]/[0.001]	15min	12W
Compound 1-d	[0.01]/[0.01]	30min	12W
Compound 1-e	[0.005]/[0.005]	30min	12W
Compound 1-f	[0.001]/[0.001]	30min	12W
Compound 1-g	[0.001]/[0.001]	30min	18W
Compound 1-h	[0.001]/[0.001]	30min	24W

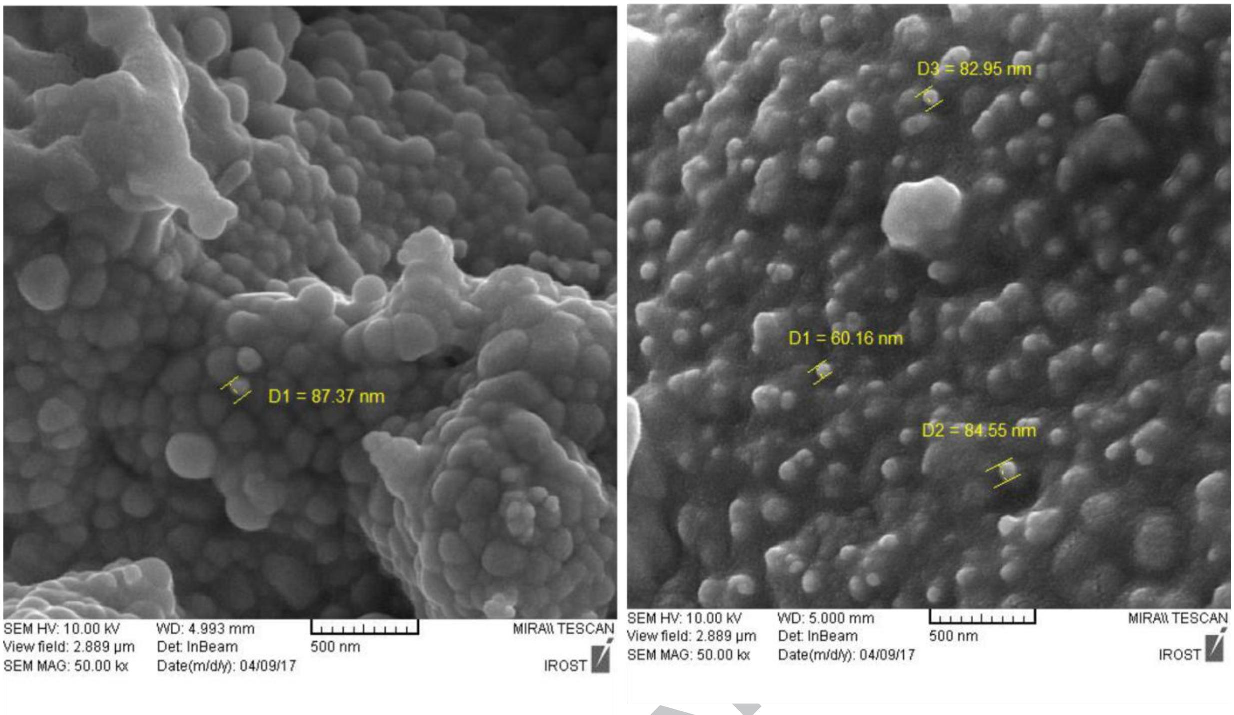

Figure 10: SEM images of CdO prepared by calcination of compound **1**

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- Compound **1**, [Cd(L1)(DMF)$_3$], as urea-functionalized MOF was synthesized.
- Effects of sonication time, sonication power 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