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(54) **MOF NANOCRYSTALS**
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CPC . Y02C 10/10; B01D 53/228; B01D 2257/504
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See application file for complete search history.

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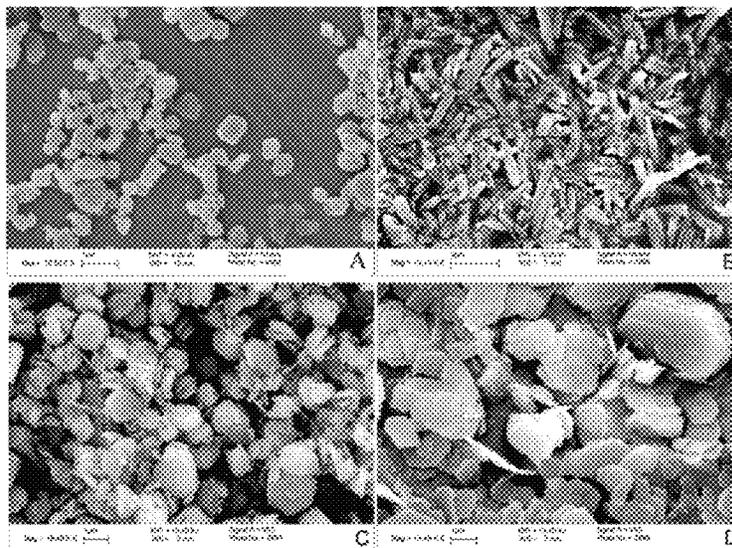
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(57) **ABSTRACT**

MOF nanocrystals having a narrow size distribution, as well as methods of making and using same are disclosed.

27 Claims, 5 Drawing Sheets



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FIGURE 1

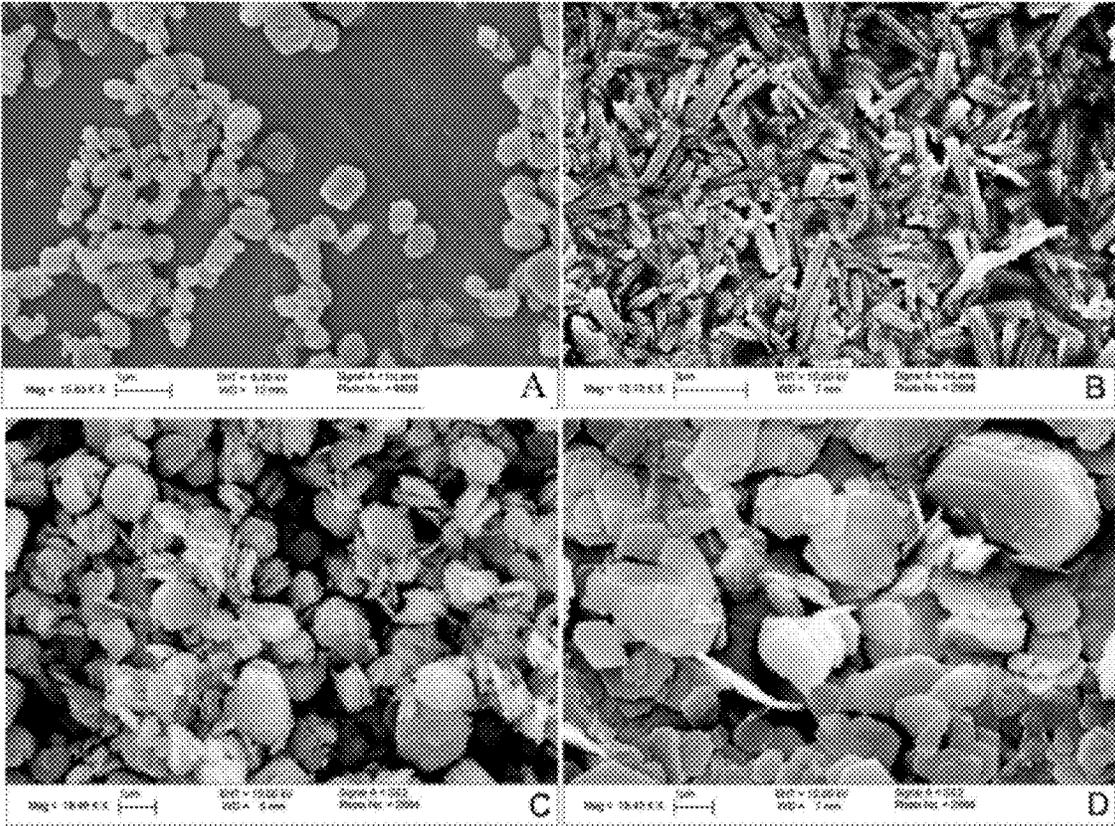


FIGURE 2

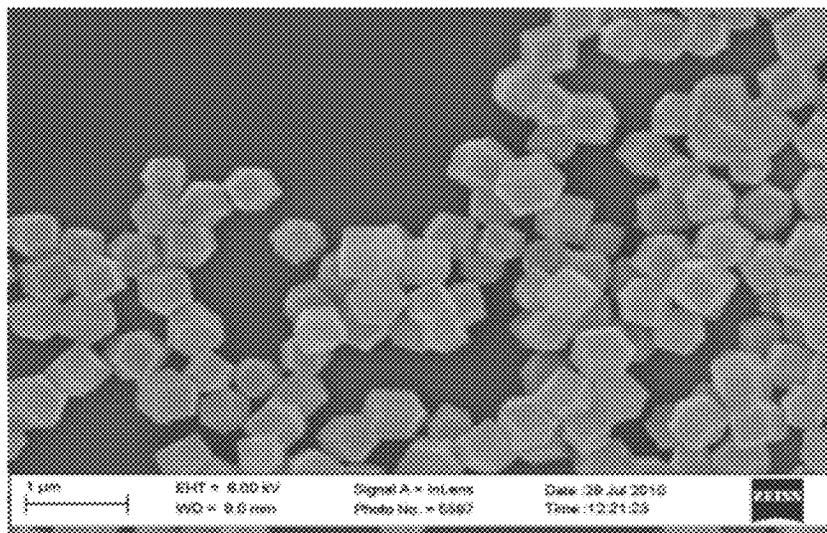


FIGURE 3

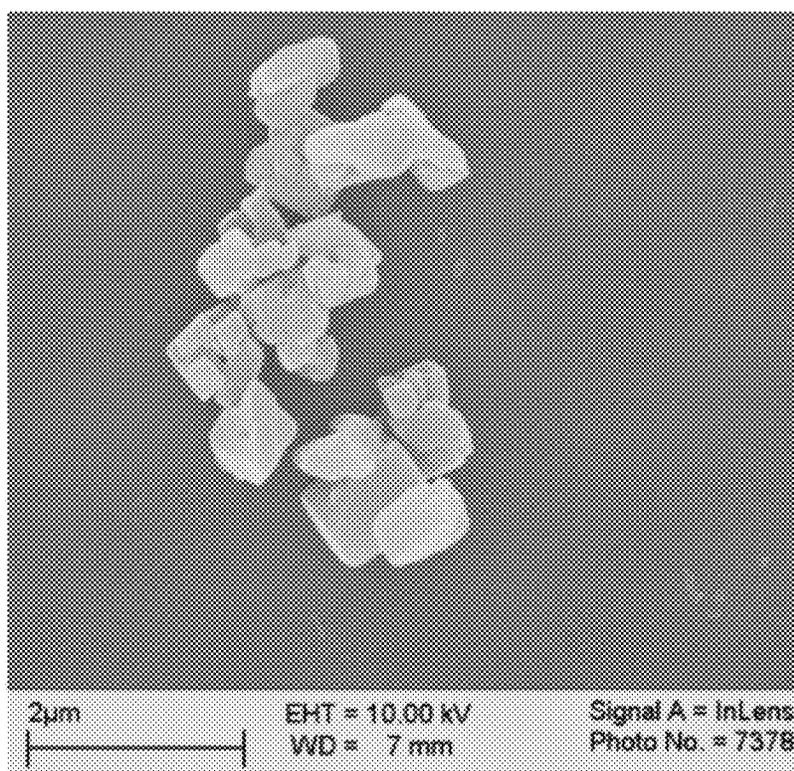


FIG 4.

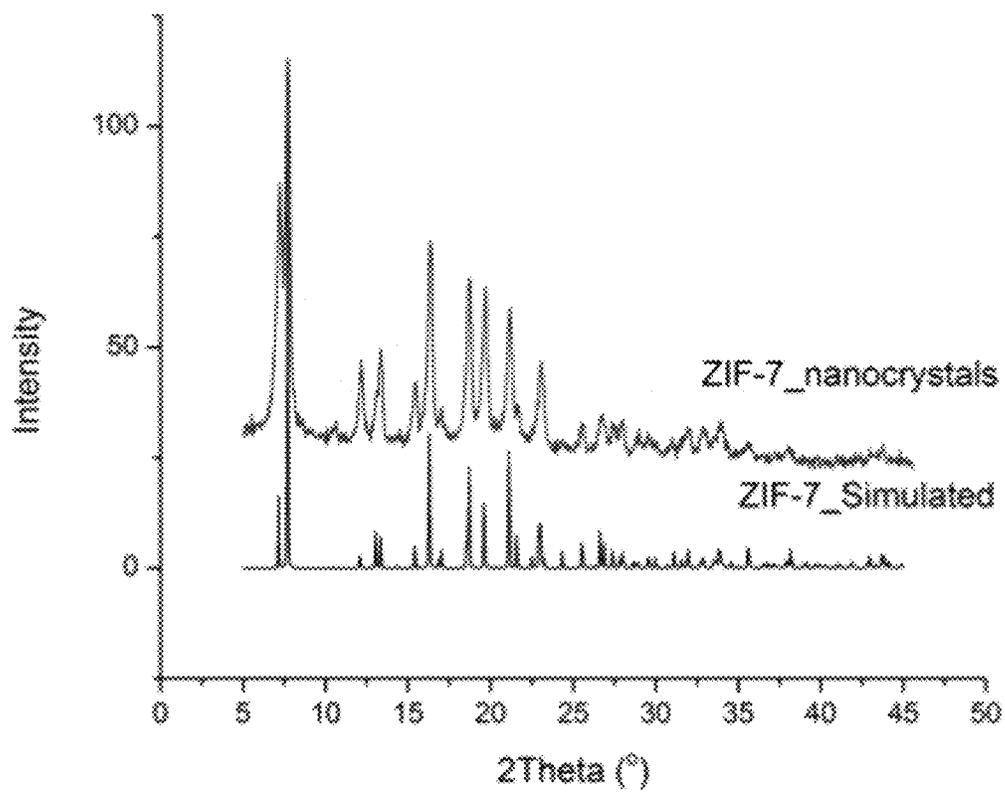


FIG. 5

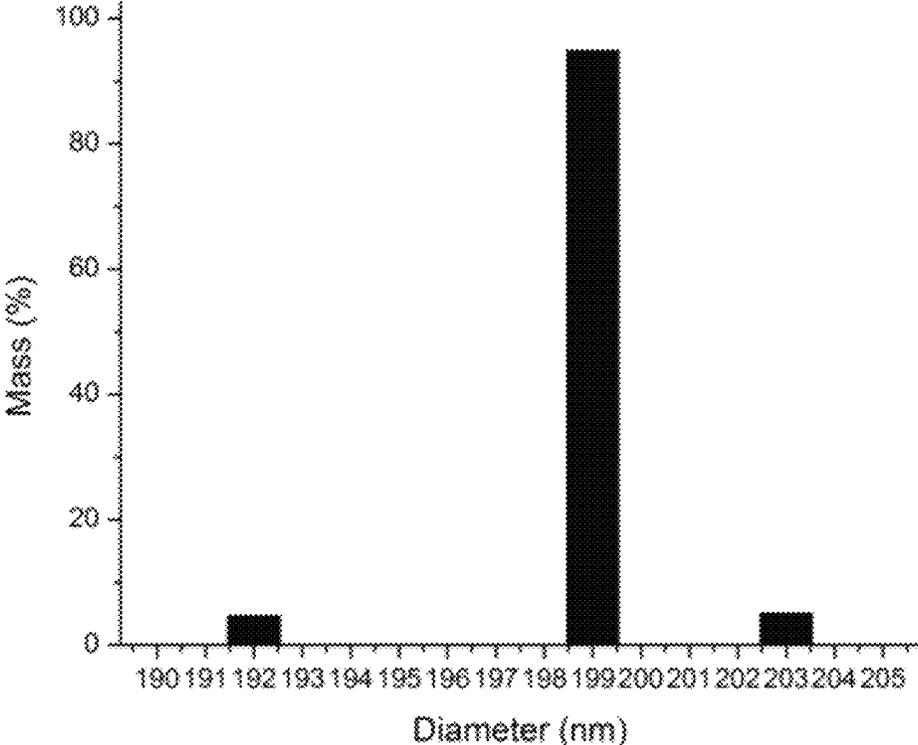
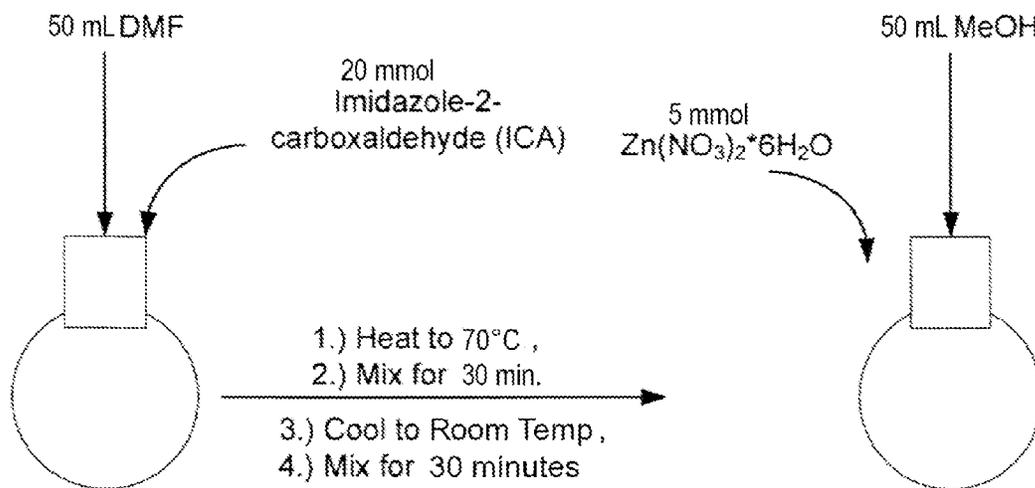
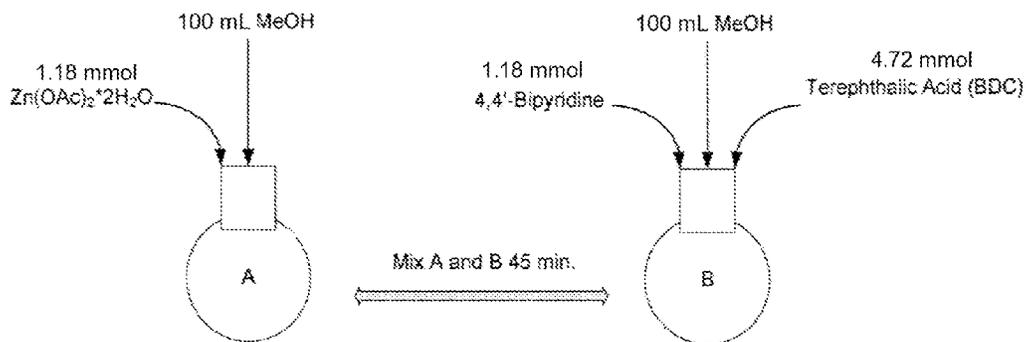


FIG. 6A



SCHEME 1

FIG. 6B



SCHEME 2

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MOF NANOCRYSTALS

PRIOR RELATED APPLICATIONS

This application claims priority to U.S. Ser. No. 61/471, 234, filed Apr. 4, 2011, and expressly incorporated herein by reference.

FEDERALLY SPONSORED RESEARCH
STATEMENT

Not applicable.

FIELD OF THE INVENTION

This invention relates to metal organic framework (MOF) materials, more particularly a method for making MOF crystals that are less than a micron in size, and thus can be called "MOF nanocrystals."

BACKGROUND OF THE INVENTION

Metal Organic Frameworks (MOFs) are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. Describing and organizing the complex structures of MOFs could be a difficult and confusing task without a logical, unambiguous set of classifications. Recently, a system of nomenclature has been developed to fill this need. The inorganic sections of a MOF, or SBUs, can be described by topologies common to several structures. Each topology, also called a net, is assigned a symbol, consisting of three lower-case letters in bold. MOF-5, for example, has a pcu net. The database of net structures can be found at the Reticular Chemistry Structure Resource (rcsr.anu.edu.au).

Based on the combination of the building blocks, the length, the combination and the functionalization of the organic linker, a large variety of pore environments can be realized. Some interesting properties the MOFs exhibit include large surface areas, and relative ease of tuning and functionalizing. Furthermore, flexibility effects within the framework may be due to weaker bonds than those of zeolites. The unique properties observed in MOFs appear to have great potential mainly in applications related with gas storage and gas separations processes. For example, MOFs can be used to make a highly selective and permeable membrane to separate small gas molecules, particularly CO₂ from CH₄. This separation is necessary for natural gas purification and CO₂ capture, it is also difficult due to the two molecules being very similar in size. However, certain MOFs are well able to separate the two gases.

Zeolitic imidazolate frameworks (ZIF) are one kind of metal-organic framework, which can also be used to reduce industrial emissions of carbon dioxide. One liter of ZIF crystals can store about 83 liters of CO₂. The crystals are non-toxic and require little energy to create, making them an attractive possibility for carbon capture and storage. Further, the porous ZIF structures can be heated to high temperatures without decomposing and can be boiled in water or solvents for a week and remain stable, making them suitable for use in hot, energy-producing environments like power plants.

In order for these various MOF materials to be used in membranes (either as MOF films or as components in mixed matrix membranes), the crystal size is preferably less than one-micron. Since solvothermal synthesis typically produces crystals larger than 10 microns, other routes are needed to

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produce smaller crystals by increasing crystal nucleation while suppressing crystal growth.

It is also desirable to control the MOF morphology. In mixed matrix membrane applications, for example, anisotropic particles would lead to alignment of particles due to the flow fields associated with producing hollow fiber membranes. This situation can be avoided if more isotropic particles are used.

The three main techniques that have been applied to reduce MOF crystal size are sonication, microwave irradiation, and addition of a base. However, there is still room in the art for improved methods to synthesize MOF nanocrystals of uniform size.

SUMMARY OF THE INVENTION

This invention describes different methods to produce sub-micron MOF crystals of that are very important for gas separation applications. Generally, crystal size is suppressed with low temperature and/or sonication or by keeping the metal ligand separate from the linker precursors until fully dissolved and then adding the metal and an optional crystallization inhibitor.

One embodiment of the invention is a method of making submicron or nanosized MOF crystals, wherein ultrasound is combined with low temperatures and a morphology control additive (2-propanol and the like) to obtain smaller more isotropic crystals. The presence of a small amount of 2-propanol substantially alters the particle morphology from needles to a more isotropic shape and improves CO₂ absorption. Therefore, the Cu-hfipbb particles produced by this approach are suitable for use in applications involving fabrication of membranes and thin films.

In a second embodiment, ZIFs are made by first dissolving the ligand precursor in DMF or other suitable solvent and mixing for a time. In a second step, both a non-solvent and the metal ions are combined with the first mixture to make small ZIF crystals with a narrower size distribution. The "non-solvent" is a liquid in which the MOF precursors have a low solubility. Hence, upon introducing the non-solvent to the mixture, the precursors are unable to stay in solution and condense quickly to form a large number of nuclei, which then act as the seeds for growing a large number of very small crystals. In absence of the non-solvent, the number of nuclei are much smaller, and over time a small number of very large crystals grow from these nuclei. The non-solvent to be used will depend upon the particular MOF and the solubility of its precursors, and it is within ordinary skill to select a suitable non-solvent for use in this method. Furthermore, we have successfully used both methanol and water in this way. We also tried ethanol. Yield was increased compared to methanol, but particle size distribution was larger (~400 nm to 1.5 microns).

In a third embodiment, MOFs are made by making separate samples of i) metal ion plus solvent and ii) ligand precursor plus solvent plus a 2-10 fold excess of linker, preferably 2-5 fold excess, more preferably a 2-4 fold excess. These two mixtures are then combined to make small MOF crystals with narrow size distribution. The idea is again to keep the metal ion and the ligand (the two main constituents of the MOF) away from each other till the point that they are quickly mixed. This leads to the instantaneous formation of many nuclei, which are all of the similar size.

In previous approaches, by contrast, the metal and the ligand are initially mixed together or added to each other

dropwise or over a period of time. This led to a large distribution in the size of nuclei and hence a large distribution in the resulting crystal sizes.

This method can also be combined with sonication, low temperatures and non-solvents to further reduce crystal size. Additionally, crystal size can be reduced by using a metal source containing a basic anion. The anion (such as acetate) induces nucleation while the excess protonated linker (terephthalic acid) inhibits growth, and is thus similar to the role of the nonsolvent.

The invention also includes the various MOF nanocrystals made according to the above methods, membranes containing same and applications using same.

By “non-solvent” herein what is meant is a liquid in which the MOF precursors have a low solubility, such that on introducing the non-solvent to the mixture, the precursors are unable to stay in solution and condense quickly to form a large number of nuclei, which are the seeds for growing a large number of very small crystals.

The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims or the specification means one or more than one, unless the context dictates otherwise.

The term “about” means the stated value plus or minus the margin of error of measurement or plus or minus 10% if no method of measurement is indicated.

The use of the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or if the alternatives are mutually exclusive.

The terms “comprise,” “have,” “include” and “contain” (and their variants) are open-ended linking verbs and allow the addition of other elements when used in a claim.

The phrase “consisting of” is a closed linking verb and does not allow the addition of any other elements.

The phrase “consisting essentially of” occupies a middle ground, allowing the addition of non material elements such as extra washes, precipitations, drying or various buffers and the like.

The following abbreviations are used herein:

BTC	1,3,5-benzenetricarboxylate
Cu[(hfpbb)(H ₂ hfpbb) _{0.5}] or Cu-hfpbb	Cu(4,4'-hexafluoroisopropylidene- bis-benzoate)
CuBTC	Cu ₃ (BTC) ₂ aka HKUST-1
DI	Deionized water
DLS	Dynamic light scattering
MIL-53(Fe)	FeIII(OH)(O ₂ C—C ₆ H ₄ —CO ₂) [Fe ₄ (OH)(O ₂ C—C ₆ H ₄ —CO ₂) ₄ per unit-cell
MOF	Metal organic framework
MOF-508b	Metal organic framework 508b
SEM	Scanning electron micrograph
SiO ₂	Silica, source Ludox AS-30 colloidal silica
XRD	Xray diffraction
ZIF	Zeolitic imidazolate framework
ZIF-7	Zeolitic imidazolate framework 7
ZIF-8	Zeolitic imidazolate framework 8
ZIF-90	Zeolitic imidazolate framework 90
ZnBTC	Zinc BTC

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1. SEM of Cu-hfpbb nanocrystal samples A-D (bar is one or three microns).

FIG. 2. SEM of ZIF-90 nanocrystals (bar is one micron).

FIG. 3. SEM of MOF-508b (bar is two microns).

FIG. 4. PXRD pattern of submicron ZIF-7 Crystals.

FIG. 5. DLS of ZIF-7 crystals.

FIGS. 6A-6B. Reaction schemes of the present invention.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

Since there is a great need in the art for small and uniform MOF crystals, we have explored various methods of making nanosized MOF crystals. The methods can best be described as variations of techniques to promote the nucleation rate and reduce the growth rate.

In the first method, we combined sonication and low temperatures (−5 to 5° C., preferably about 0° C.) together with a morphology control additive (such as methanol, ethanol, 2-propanol and the like), in order to make submicron isotropic crystals of Cu-hfpbb.

We have also made uniform submicron ZIF-90 crystals using the “non-solvent” approach by separately adding both solvated metal and a non-solvent to pre-dissolved ligand in solvent mixture.

Finally, we have made MOFs by making a separate metal plus solvent mixture and a separate ligand precursor plus linker plus solvent mixture and then combining these two mixtures. Thus, in both cases, holding back the metal ions until the ligands and linkers were solvated, allowed a uniform size distribution of crystals to be made. A non-solvent can also be used in this method, as can low temperatures and sonication.

Another embodiment of the invention is a method of making nanosized MOF crystals comprising growing MOF crystals and increasing crystal nucleation, such that isotropic MOF crystals of average size less than one micron and a size distribution of less than +/-20% are obtained. Crystal nucleation is increased by keeping metal ions and ligand precursors separated until fully solvated and then quickly bringing them together or by agitation together with a crystal growth inhibitor and/or low temperatures or combinations thereof.

Membranes made with the MOF crystals are also enabled herein, wherein membranes can be made according to known methods in the art, including fabrication of continuous MOF membranes via secondary growth, by placing (or depositing) seed crystals onto e.g., a porous support followed by solvothermal treatment to grow them into a continuous MOF membrane. Other methods include incorporation of the MOF crystals into mixed-matrix gas-separation membranes, such as ZIF-90/6FDA-DAM membranes, or incorporation into hollow fibers or by film casting methods, and the like.

Methods of separating gases are also provided herein, the methods generally comprising subjecting a mixture of gases to the membranes made herein, and separating CO₂ from said mixture of gases, wherein said mixture of gases includes CO₂ plus at least one gas selected from H₂, N₂, CH₄, O₂ and combinations thereof. Other applications include gas separation, catalysis, drug delivery, optical and electronic applications, and sensing applications.

The following examples are illustrative only, and are not intended to unduly limit the scope of the invention.

EXAMPLE 1

Cu-hfpbb

Cu-hfpbb is a MOF composed of one dimensional cages (5.1 Å) joined by small windows (3.1 Å) with an exceptionally high predicted CO₂/CH₄ selectivity (~1000). The synthesis of Cu-hfpbb has several unusual features in comparison to most other MOFs. First, the control of hydrothermal synthesis is impeded by the marked hydrophobicity of one of the

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main reactants, H₂hfipbb. Only above 90° C. does one observe a solubility of H₂hfipbb high enough to form a clear aqueous solution. Second, the MOF formation requires a protonated H₂hfipbb ligand. Most MOF syntheses rely on a base to deprotonate a carboxylic acid, which then becomes incorporated into the MOF and creates a basic environment inside the MOF. As a result of these unique features, attempts to solvothermally synthesize Cu-hfipbb in an aprotic solvent (such as N,N-dimethylformamide) have unsuccessful. These two factors precluded the use of conventional methods to synthesize sub-micron Cu-hfipbb.

Because the published hydrothermal synthesis conditions result in crystals that are too large for membrane synthesis (~100/μm), one research group explored crystal synthesis by adding several organic solvents (e.g. methanol, ethanol, acetone, and dimethylformamide) to the Cu-hfipbb reaction mixture and found that methanol-water mixtures produced crystals with lower aspect ratios—in other word the crystals were less elongated and more isotropic.^{3,4} However, nanocrystals were not obtained with any of the examined growth conditions.

Submicron sized Cu-hfipbb was made in this example by combining low temperature crystal growth, ultrasound sonication and a morphology control additive to control crystal shape. By using sonication at 0° C. combined with a morphology control additive (2-propanol), submicron crystals of Cu-hfipbb were produced (FIG. 1).

DLS was performed to determine the average particle size of 660 nm with a 84 nm standard deviation (data not shown). The yields obtained were 0.13 grams of crystals per gram of ligand and 0.31 grams of crystals per gram of copper (II) nitrate used. This is the first reported synthesis of submicron Cu-hfipbb particles.

In more detail, reagents were used as purchased. 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (98%), copper (II) nitrate hemi(pentahydrate) (98%), and 2-propanol (99.5%) were purchased from SIGMA-ALDRICH.™ To synthesize Cu[(hfipbb)(H₂hfipbb)_{0.5}], 200 mg of H₂hfipbb was dispersed in 75 mL of deionized water by shaking and sonication. In a separate container, 79 mg of copper(II) nitrate hemi(pentahydrate) was dissolved in a 5 mL of water separately and added immediately before sonication. The molar ratio of copper nitrate to H₂hfipbb to water was 1:1.5:12900.

All syntheses were sonicated at intervals of 1 second on and 1 second off. Sonication was carried out with a SONICS VIBRACELL™ VCX 130 source equipped with a Model CV 18 horn operating at 20 kHz. Our detailed parametric studies are illustrated by four representative experimental conditions (labeled A-D and summarized in Table 1).

TABLE 1

Summary of synthesis conditions for the 4 samples of Cu[(hfipbb)(H ₂ hfipbb) _{0.5}]				
	A	B	C	D
Synthesis time (hrs)	6	6	6	1
Temperature (° C.)	0	0	0	90
Percent 2-propanol	1.2	0	1.2	1.2
Sonication power (W)	91	91	26	91

For reaction conditions A, C, and D, 1 mL of 2-propanol was added. For reactions A, B, and D, the sonicating power was set at 91 W, and for reaction C it was set at 26 W. For syntheses A, B, and C, the reaction vessel was maintained inside a 3 L block of ice to keep the reaction temperature close to 0° C. for the 6.6 hour duration of the experiment. For

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synthesis D, the reaction container was placed on a hot plate and heated to 90° C. prior to and during the synthesis for 1 hour.

After synthesis, all samples were centrifuged and washed with 2-propanol to remove excess H₂hfipbb, and then washed in water. For purposes of comparison, Cu-hfipbb was also synthesized by the previously published hydrothermal method.

X-ray diffraction data were collected on a well aligned PANALYTICAL X'PERT PRO™ MPD with Cu Kα radiation (45 kV, 40 mA) and an X'CELERATOR™ detector. Pawley fits of the unit cell were carried out using the ACCELERYS™ package in MATERIALS STUDIO.™ Scanning electron microscopy (SEM) images were collected on a LEO1530™ operating at 10 kV. Light scattering measurements were made on a BROOKHAVEN INSTRUMENTS™ BI-APD detector equipped with a 632.8 nm/75 mW laser, using samples that were dispersed in hexane and with oleic acid added as a surfactant.

All samples were filtered through a 5 μm filter prior to DLS measurements. Thermogravimetric measurements were made on a NETZCH™ STA 449 F1 Jupiter with a AEO-LOS™ QMS 403 C mass spectrometer with a heating rate of 10° C./min. CO₂ adsorption was carried out on a HIDEN-ISOHEMA™ Intelligent Gravimetric Analyzer at 25° C. after activation for 4 hours under vacuum at 200° C.

TABLE 2

Summary of results from Dynamic Light Scattering measurements.				
	A	B	C	D
Percent yield (%)	11	7	7	40
Average size (nm)	660	692	794	571; 1713 ^a
Standard deviation (nm)	84	89	140	172; 589 ^a
Scattering % < 1 μm	88	80	80	49 ^b

^aThe size and standard deviation of both distributions of Sample D are shown, as they were comparable in size.

^bMuch of the sample appeared to have been trapped in the 5 μm filter and the true fraction of sub-micron particles may be even lower.

Scanning electron micrographs of samples from experimental conditions A-D are shown in FIG. 1. Sample A is the representative result that clearly shows the formation of sub-micron particles of Cu-hfipbb. The powder X-ray diffraction patterns from all four conditions A-D (not shown) show that Cu-hfipbb is produced. Only sample A, however, consists of pure Cu-hfipbb; samples B-D also contained a small amount of impurity phase associated with XRD peaks at 6.6, 8.7, and 11.5° 2θ. Although the assignment of these impurity peaks is currently unclear, it is worth noting that the impurity phase can also be synthesized by using the reaction conditions for sample A with stirring and no sonochemical energy input.

The yield of Cu-hfipbb in sample A was approximately 11% (Table 2). The yield for all syntheses was lower in comparison to other reports of sonochemically synthesized MOFs and of conventionally synthesized Cu-hfipbb. A number of factors may contribute to this reduced yield. A stoichiometric ratio of metal to ligand (1:1.5) was used, as opposed to other syntheses that used up to a four-fold excess of H₂hfipbb. In addition, the lack of solubility of H₂hfipbb in water meant that the amount of reactant in solution was low in comparison to sonochemical syntheses of other MOFs in which the ligand is dissolved in a suitable solvent. Sample D, synthesized at an elevated temperature, produced a yield of 40%, comparable to that of hydrothermal syntheses. For the other samples, the use of low temperature was designed to reduce the growth rate of the crystallites after crystal nucleation.

In summary, the growth rate appears to be controlled by the temperature, with higher temperatures resulting in a larger distribution of particle sizes. The phase purity of the crystal structure appears to be affected primarily by the sonicating power, but also by the presence of elevated temperatures during sonication. The particle geometry is influenced by the presence of 2-propanol, which acts as a “crystal-shape-directing” agent. In the absence of 2-propanol, Cu-hfipbb grows as long needle-like particles, but more isotropic particles are formed upon the addition of 1.2% 2-propanol.

The yields from the present method are comparable with those from hydrothermal synthesis on the basis of the amount of ligand used. The porosity and CO₂ uptake capacity of the sample is not reduced by sonochemical synthesis, indeed CO₂ capacity is somewhat improved on our crystals from 1.0 molecules of CO₂ per unit cell (0.76 mmol/g) for the hydrothermally synthesized sample to 1.1 molecules per unit cell (0.87 mmol/g) for sample A at 10 bar (data not shown).

Due to their sub-micron size and more isotropic shape, wherein a significant fraction of surface area exposes the nanopores of the material for uptake of gases, the present particles of Cu-hfipbb are suitable for use in membrane applications for the separation of gas and hydrocarbon mixtures.

It is hypothesized that the above method of crystal growth could be applied to additional carboxylate-based MOFs, because the sonication can increase nucleation while the low temperatures suppress the growth rate of the nuclei. Thus, the method has general applicability.

EXAMPLE 2

ZIF-90

ZIF-90 is a material composed of Zinc atoms linked through imidazolite carboxyaldehyde linkers to form a sodalite cage structure with 3.5 Å windows that has been shown to preferentially adsorb CO₂ over CH₄.

A closely related MOF, ZIF-8 was previously synthesized by mixing excess ligand with Zn at room temperature in methanol, but an analogous procedure for ZIF-90 did not yield small crystals due to the decreased solubility of the imidazole carboxyaldehyde linker in methanol. Furthermore, this ligand is soluble in DMF only after heating for at least 30 minutes.

One lab recently reported a ZIF-90 synthesis by heating the metal/ligand precursors in DMF and then adding a “non-solvent” to the cooled DMF solution, thus precipitating sub-micron ZIF-90 crystals. However, this method led to a size distribution with both small crystals of about 100 nm and larger crystals around 1 micron in size. One possible explanation for this size distribution is that prior to the addition of non-solvent, the metal and ligand were already coordinated forming particles with various sizes that grow non-uniformly until addition of non solvent.

We have now discovered a method to make uniform sub-micron ZIF-90 crystals using the “non-solvent” approach by separately adding the solvated metal and non-solvent to the dissolved DMF plus ligand mixture (Scheme 1 as depicted in FIG. 6A). This method prevents the formation of particles until the addition of non-solvent. Prior to addition of non-solvent, only solvated ligands and metals exist in solution instead of coordinated metals and ligands as in the synthesis of Bae et al. By separating the zinc (or other metal) and imidazole carboxyaldehyde until the time of mixing in the non-solvent, small ZIF-90 crystals can be synthesized much quicker with a very narrow size distribution.

Based on DLS, the ZIF-90 particles made herein had an average size of 380 nm with a 16 nm standard deviation. The yield was 0.04 gram and 0.06 grams of crystals formed per gram of imidazole carboxyaldehyde ligand and zinc used, respectively.

EXAMPLE 3

MOF-508b

MOF-508b is another small-pore MOF consisting of zinc atoms linked via terephthalate and pillared with bipyridyl ligands to form 4 Å 1D channels.^{10,11} While nanocrystals of this material could be synthesized by adding a base, such as triethylamine, it was difficult to isolate the proper phase as the subsequent triethylammonium ions can be incorporated in anionic frameworks as charge balancing ions.

Another group used a similar method with cobalt hydroxide as the metal base source to fabricate cobalt succinates to create phase diagrams, but no nanocrystals were reported. Instead of adding another chemical species to the reaction mixture (such as triethylamine), we have developed an approach that incorporated a metal salt with a basic anion; thereby, eliminating salt byproducts and suppressing formation of additional phases.

Specifically, nanocrystals of MOF-508b (Scheme 2 as depicted in FIG. 6B) could be formed at room temperature in methanol when using between 2 and 4 fold excess of terephthalic acid linker. Using the Smartiff software package to analyze MOF 508b crystals from SEM images, the average crystal size obtained was 832 nm with a 45 nm standard deviation (FIG. 3). This synthetic route produced 0.23 grams of crystals per gram of Zinc Acetate and 0.06 grams of crystals per gram of terephthalic acid used, respectively. This is the first reported synthesis of MOF-508b nanoparticles.

The MOF nanocrystals prepared herein can be used for any use that MOF crystals have traditionally been used for. One particular use is to make molecular sieve membranes, which can be used, e.g., for CO₂ removal e.g., from refinery or chemical plant waste or natural gas usage.

EXAMPLE 4

ZIF-7

In addition to ZIF-90, the nonsolvent method can also be used to synthesize ZIF-7 nanocrystals. ZIF-7 is a small-pore MOF material composed of zinc metal centers linked via benzimidazole ligands.¹⁰ In a previous report, ZIF-7 nanocrystals were formed after suspending benzimidazole and zinc nitrate hexahydrate in DMF for 48 hours.¹¹

Using our nonsolvent method, nanocrystals of ZIF-7 are synthesized by first dissolving 20 mmol of benzimidazole in 50 mL DMF followed by addition of 5 mmol zinc nitrate hexahydrate dissolved in 50 mL methanol. After mixing the DMF/benzimidazole and Methanol/Zinc solutions for 1 hr under vigorous stirring, phase-pure ZIF-7 nanocrystals are formed (see expected PXRD pattern in FIG. 4). The nonsolvent method produces ZIF-7 crystals approximately 199 nm with a 5 nm standard deviation based on DLS measurements (see FIG. 5). The yield of the synthesis is 0.33 gram and 0.53 gram of crystals formed per gram of benzimidazole ligand and Zinc used, respectively.

The following references are incorporated by reference in their entirety.

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What is claimed is:

1. A method for preparing uniformly small MOF crystals, comprising the step of growing a MOF crystal with ultrasound at a temperature of -5 to 5° C. with a morphology control additive for a period of time so as to obtain isotropic MOF crystals of average size less than one micron and a size distribution of less than $\pm 20\%$.

2. The method of claim 1, wherein the morphology control additive is ethanol, or 2-propanol.

3. The method of claim 1, wherein size distribution is less than $\pm 10\%$.

4. The method of claim 1, wherein size distribution is less than $\pm 5\%$.

5. The method of claim 1, wherein the MOF is Cu(4,4'-hexafluoroisopropylidene-bis-benzoate) and the control additive is 2-propanol.

6. A method for preparing uniformly small MOF crystals, comprising:

- a) dissolving the ligand precursor in a suitable solvent and mixing;
- b) adding a non-solvent (for said ligand precursor) to the mixture in step a) and mixing;
- c) adding metal ions to the mixture in step b) and mixing, so as to make MOF crystals of average size less than one micron and the size distribution is less than $\pm 20\%$.

7. The method of claim 6, wherein size distribution is less than $\pm 10\%$.

8. The method of claim 6, wherein size distribution is less than $\pm 5\%$.

9. The method of claim 6, wherein the non-solvent is methanol or water.

10. The method of claim 6, wherein the MOF is ZIF-90 and the non-solvent is methanol.

11. The method of claim 6, wherein the MOF is ZIF-7 and the non-solvent is methanol.

12. A method for preparing uniformly small MOF crystals, comprising

- a) making a mixture of metal ion plus solvent;
- b) making a separate mixture of ligand precursor plus solvent plus 2-4 fold excess of linker;
- c) quickly combining samples a) and b) and mixing, so as to make MOF crystals of average size less than one micron and a size distribution of less than $\pm 20\%$.

13. The method of claim 11, wherein the size distribution is less than $\pm 10\%$.

14. The method of claim 11, wherein the size distribution is less than $\pm 5\%$.

15. The method of claim 11, wherein the MOF is MOF508b.

16. The method of claim 11, wherein the metal ion is a metal anion.

17. The method of claim 11, wherein the metal ion is a metal acetate.

18. A composition of MOF crystals that are less than one micron in average size (without having been size reduced after synthesis) and have a size distribution of less than $\pm 20\%$.

19. The composition of claim 18, having a size distribution of less than $\pm 10\%$.

20. A membrane comprising Cu(4,4'-hexafluoroisopropylidene-bis-benzoate) crystals of less than one micron average size (that are not size reduced after synthesis) plus a porous support.

21. A membrane comprising MOF508b crystals of less than one micron average size (that are not size reduced after synthesis) plus a porous support.

22. A membrane comprising ZIF-90 crystals of less than one micron average size (that are not size reduced after synthesis) plus a porous support.

23. A membrane comprising ZIF-7 crystals of less than one micron average size (that are not size reduced after synthesis) plus a porous support.

24. A method for preparing uniformly small MOF crystals, comprising the steps of:

- a) growing a MOF crystal with sonication at a temperature of -5 to 5° C. with a morphology control additive selected from ethanol or 2-propanol for a period of time; or
- b) b1) dissolving the ligand precursor in a suitable solvent and mixing for a time, b2) separately adding a non-solvent (for said ligand precursor) and metal ions with the mixture in step b1) and growing MOF crystals for a period of time; or
- c) c1) making a mixture of metal ion plus solvent, c2) making a separate mixture of ligand precursor plus solvent plus 2-5 fold excess of linker, quickly combining mixtures c1) and c2) and growing MOF crystals for a period of time; and
- d) said period of time sufficient to obtain isotropic MOF crystals of average size less than one micron and a size distribution of less than $\pm 20\%$.

25. A membrane comprising uniformly small MOF crystals, comprising the steps of:

- a) growing a MOF crystal with sonication at a temperature of -5 to 5° C. with a morphology control additive selected from ethanol or 2-propanol for a period of time; or
- b) b1) dissolving the ligand precursor in a suitable solvent and mixing for a time, b2) separately adding a non-solvent (for said ligand precursor) and metal ions with the mixture in step b1) and growing MOF crystals for a period of time; or
- c) c1) making a mixture of metal ion plus solvent, c2) making a separate mixture of ligand precursor plus solvent plus 2-5 fold excess of linker, quickly combining mixtures c1) and c2) and growing MOF crystals for a period of time; and
- d) said period of time sufficient to obtain isotropic MOF crystals of average size less than one micron and a size distribution of less than $\pm 20\%$.

26. A method of separating CO_2 from other gases, comprising subjecting a mixture of gases to the membrane of claim 25, and separating CO_2 from said mixture of gases, wherein said mixture of gases includes CO_2 plus at least one gas selected from H_2 , N_2 , CH_4 , O_2 and combinations thereof.

27. A method of making nanosized MOF crystals, said method comprising growing MOF crystals and increasing crystal nucleation, such that isotropic MOF crystals of average size less than one micron and a size distribution of less than $\pm 20\%$ are obtained, wherein crystal nucleation is

increased by keeping metal ions and ligand precursors separated until fully solvated and then quickly bringing them together or by agitation plus a crystal growth inhibitor or combinations thereof.

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