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Various Applications of MOFS, from Nanodampers to probable Vaccine Materials for COVID-19: A Review

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ABSTRACT

Metal-Organic Frameworks (MOFs) form a family of porous inorganic-organic ordered hybrid materials which have generated huge interest in the scientific community. Whilst magnetic, catalytic and drug delivery properties have been largely documented, the basic mechanical and immunization properties of these materials have not received as much interest. The present paper reviews its various properties and suitability and as it also provides immunization so it may be considered as vaccine material for various viral diseases like COVID-19.

Keywords: *Nanodampers,Springs,Catalysts,Porosity,COVID-19*

INTRODUCTION

Metal Organic Frameworks (MOF), are a family of organized inorganic-organic porous materials which have generated a large interest in the scientific community and are composed of two major components: A metal ion or cluster of metal ions and an organic molecule called a linker. For this reason, the materials are often referred to as hybrid organic–inorganic materials The choice of metal and linker dictates the structure and hence properties of the MOF. For example, the metal's coordination preference influences the size and shape of pores by dictating how many ligands can bind to the metal and in which orientation (BOEE, 2004).

Since ligands in MOFs typically bind reversibly, the slow growth of crystals often allows defects to be re-dissolved, resulting in a material with millimeter-scale crystals and a near-equilibrium defect density. Solvo thermal synthesis is useful for growing crystals suitable to structure determination, because crystals grow over the course of hours to days. Some of the uses or applications of MOF's has been studied.

MATERIALS AND METHODS

For this, we visited more than several webpages returned from a google search on various applications of MOFS, from Nanodampers to probable vaccine materials for COVID-19 were attempted. The links of some of which are https://anr.fr/Project-ANR-12-BS10-0005.,https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5952545/.,https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5952545/.,https://www.nanowerk.com/mof-metal-organic-framework.php., https:// onlinelibrary.wiley.com/doi/10.1002/adfm.201600650., https://journals.iucr.org/a/issues/2018/a1/00/a56866/a56866.pdf., https://www.healthline.com/health-news/heres-exactly-where-were-at-with-vaccines-and-treatments-for covid., https://onlinelibrary.wiley.Com/doi/10.1002/adfm.201600650., Katihar Engg. College official WhatsApp Group.

The main aim of this review paper is to contribute a knowledge related to present pandemic in the light of more knowledge with an privilege to combat with COVID-19 and successful human race.

RESULTS AND DISCUSSION

Usage / Applications of MOF:

Altogether 13 usage/applications of MOF have been presented and discussed.

(1) MOF as Shock Absorber or Springs Metal Organic Frameworks (MOF):

They are a family of organized inorganic-organic porous materials which have generated a large interest in the scientific community. Whilst many properties of these materials have been largely studied, their basic mechanical properties has received little attention. However, as several MOF structures are highly flexible, it is thought that such solids can be used as shock-absorbers or springs.

It was established that the inclusion of n-alkane in MOF{MIL-53(Cr)}allows a fully reversible structural switching under compression–decompression with the absence of any hysteresis which makes this guest loaded system potentially interesting for nano-spring applications. To complement this, conftning polar molecules into the pores leads to an irreversible structure transformation with an asso-ciated absorbed energy of 4 J g^{-1} for the water-loaded MIL-53(Cr) which outperforms other nanoporous materials reported so far. Interestingly this latter system is promising in terms of manufacturing novel shock nano-absorbers. Incorporating guest molecules of different polarities and strength interactions with the pore wall allows a massive extension of the storage abilities of this flexible material which has been previously evoked as nano-dampers by virtue of its reversible structural transition with the presence of a large hysteresis in its empty state. Such a modulation of the mechanical properties of this fexible MOF might be also envisaged by granting the organic linker with different polar/apolar functions and by changing the nature of the metal center. This will guide the next step of our investigation on this system.

(2) MOF as Hydrogen Storage Materials:

Molecular hydrogen has the highest specific energy of any fuel. However unless the hydrogen gas is compressed, its volumetric energy density is very low, so the transportation and storage of hydrogen require energy-intensive compression and liquefaction processes. MOFs attract attention as materials for adsorptive hydrogen storage because of their high specific surface areas and surface to volume ratios, as well as their chemically tunable structures.

Compared to an empty gas cylinder, a MOF-filled gas cylinder can store more hydrogen at a given pressure because hydrogen molecules adsorb to the surface of MOFs. Furthermore, MOFs are free of dead-volume, so there is almost no loss of storage capacity as a result of space-blocking by non-accessible volume. Also, because the hydrogen uptake is based primarily on physisorption, many MOFs have a fully reversible uptake-and-release behavior. No large activation barriers are required when liberating the adsorbed hydrogen. The storage capacity of a MOF is limited by the liquid-phase density of hydrogen because the benefits provided by MOFs can be realized only if the hydrogen is in its gaseous state.

Adsorption is the process of trapping atoms or molecules that are incident on a surface; therefore the adsorption capacity of a material increases with its surface area. In three dimensions, the maximum surface area will be obtained by a structure which is highly porous, such that atoms and molecules can access internal surfaces. This simple qualitative argument suggests that the highly porous metal-organic frameworks (MOFs) should be excellent candidates for hydrogen storage devices.

(3) MOF as Catalysts:

MOFs have potential as heterogeneous catalysts, although applications have not been commercialized Their high surface area, tunable porosity, diversity in metal and functional groups make them especially attractive for use as catalysts. Zeolites are extraordinarily useful in catalysis. Zeolites are limited by the fixed tetrahedral coordination of the Si/Al connecting points and the two-coordinated oxide linkers. In contrast with this limited scope, MOFs exhibit more diverse coordination geometries, polytopic linkers, and ancillary ligands (F^-, OH^-, H_2O among others). It is also difficult to obtain zeolites with pore sizes larger than 1 nm, which limits the catalytic applications of zeolites to relatively small organic molecules (typically no larger than xylenes). Furthermore, mild synthetic conditions typically employed for MOF synthesis allow direct incorporation of delicate functionalities into the framework structures. Such a process would not be possible with zeolites or other microporous crystalline oxide-based materials because of the harsh conditions typically used for their synthesis (*e.g.*, calcination at high temperatures to remove organic templates). Metal-Organic Framework MIL-101 is one of the most used MOFs for catalysis incorporating different transition metals such as Cr (BOEE, 2004 and Biinzli, 2010).

(4) Biological Imaging and Sensing:

A potential application for MOFs is biological imaging and sensing via photoluminescence. A large subset of luminescent MOFs use lanthanides in the metal clusters. Lanthanide photoluminescence has many unique properties that make them ideal for imaging applications, such as characteristically sharp and generally non-overlapping emission bands in the visible and near-infrared (NIR) regions of the spectrum, resistance to photobleaching or 'blinking', and long luminescence lifetimes. However, lanthanide emissions are difficult to sensitize directly because they must undergo LaPorte forbidden f-f transitions. Indirect sensitization of lanthanide emission can be accomplished by employing the "antenna effect," where the organic linkers act as antennae and absorb the excitation energy, transfer the energy to the excited state of the lanthanide, and yield lanthanide luminescence upon relaxation. A prime example of the antenna effect is demonstrated by MOF-76, which combines trivalent lanthanide ions and 1,3,5-benzenetricarboxylate (BTC) linkers to form infinite rod SBUs coordinated into a three dimensional lattice As demonstrated by multiple research groups, the BTC linker can effectively sensitize the lanthanide emission, resulting in a MOF with variable emission wavelengths depending on the lanthanide identity. Additionally, the Yan group has shown that Eu^{3+}- and Tb^{3+}- MOF-76 can be used for selective detection of acetophenone from other volatile monoaromatic hydrocarbons. Upon acetophenone uptake, the MOF shows a very sharp decrease, or quenching, of the luminescence intensity.

For use in biological imaging, however, two main obstacles must be overcome:

- MOFs must be synthesized on the nanoscale so as not to affect the target's normal interactions or behavior

- The absorbance and emission wavelengths must occur in regions with minimal overlap from sample auto fluorescence, other absorbing species, and maximum tissue penetration.

Regarding the first point, nanoscale MOF (NMOF) synthesis has been mentioned in an earlier section. The latter obstacle addresses the limitation of the antenna effect. Smaller linkers tend to improve MOF stability, but have higher energy absorptions, predominantly in the ultraviolet (UV) and high-energy visible regions. A design strategy for MOFs with redshifted absorption properties has been accomplished by using large, chromophoric linkers. These linkers are often composed of polyaromatic species, leading to large pore sizes and thus decreased stability. To circumvent the use of large linkers, other methods are required to redshift the absorbance of the MOF so lower energy excitation sources can be used. Post-synthetic modification (PSM) is one promising strategy. Luo et al. introduced a new family of lanthanide MOFs with functionalized organic linkers. The MOFs, deemed MOF-1114, MOF-1115, MOF-1130, and MOF-1131, are composed of octahedral SBUs bridged by amino functionalized dicarboxylate linkers. The amino groups on the linkers served as sites for covalent PSM reactions with either salicylaldehyde or 3-hydroxynaphthalene-2-carboxyaldehyde. Both of these reactions extend the π-conjugation of the linker, causing a redshift in the absorbance wavelength from 450 nm to 650 nm. The authors also propose that this technique could be adapted to similar MOF systems and, by increasing pore volumes with increasing linker lengths, larger pi-conjugated reactants can be used to further redshift the absorption wavelengths. Biological imaging using MOFs has been realized by several groups, namely Foucault-Collet and co-workers. In 2013, they synthesized a NIR-emitting Yb^{3+}-NMOF using phenylenevinylene dicarboxylate (PVDC) linkers. They were observed cellular uptake in both HeLa cells and NIH-3T3 cells using confocal, visible, and NIR spectroscopy. Although low quantum yields persist in water and Hepes buffer solution, the luminescence intensity is still strong enough to image cellular uptake in both the visible and NIR regimes.

(5) Nuclear Waste form Materials:

The development of new pathways for efficient nuclear waste administration is essential in wake of increased public concern about radioactive contamination, due to nuclear plant operation and nuclear weapon decommission. Synthesis of novel materials capable of selective actinide sequestration and separation is one of the current challenges acknowledged in the nuclear waste sector. Metal–organic frameworks (MOFs) are a promising class of materials to address this challenge due to their porosity, modularity, crystallinity, and tunability. Porosity of MOFs can be used to incorporate contained guest molecules and trap them in a structure by installation of additional or capping linkers.

(6) Drug Delivery Systems:

The synthesis, characterization, and drug-related studies of low toxicity, biocompatible MOFs has shown that they have potential for medical applications. A variety of methods exist for inducing drug release, such as pH-response, magnetic-response, ion-response, temperature-response, and pressure response. In 2010 Smaldone *et al.*, an international research group, synthesized a biocompatible MOF termed CD-MOF-1 from cheap edible natural products. CD-MOF-1 consists of repeating base units of 6 γ-cyclodextrin rings bound together by potassium ions. γ-cyclodextrin (γ-CD) is a symmetrical cyclic oligosaccharide that is mass-produced enzymatically from starch and consists of eight asymmetric α-1,4-linked D-glucopyranosyl residues. The molecular structure of these glucose derivatives, which approximates a truncated cone, bucket, or torus, generates a hydrophilic exterior surface and a nonpolar interior cavity. Cyclodextrins can interact with appropriately sized drug molecules to yield an inclusion complex. Smaldone's group proposed a cheap and simple synthesis of the CD-MOF-1 from natural products. They dissolved sugar (γ-cyclodextrin) and an alkali salt (KOH, KCl, potassium benzoate) in distilled bottled water and allowed 190 proof grain alcohol (Everclear) to vapor diffuse into the solution for a week. The synthesis resulted in a cubic (γ-CD) 6 repeating motif with a pore size of approximately 1 nm. Subsequently, in 2017 Hartlieb *et al*., at Northwestern did further research with CD-MOF-1 involving the encapsulation of ibuprofen. The group studied different methods of loading the MOF with ibuprofen as well as performing related bioavailability studies on the ibuprofen-loaded MOF. They investigated two different methods of loading CD-MOF-1 with ibuprofen; crystallization using the potassium salt of ibuprofen as the alkali cation source for production of the MOF, and absorption and deprotonation of the free-acid of ibuprofen into the MOF. From there the group performed in vitro and in vivo studies to determine the applicability of CD-MOF-1 as a viable delivery method for ibuprofen and other NSAIDs. In vitro studies showed no toxicity or effect on cell viability up to 100 μM. In vivo studies in mice showed the same rapid uptake of ibuprofen as the ibuprofen potassium salt control sample with a peak plasma concentration observed within 20 minutes, and the cocrystal has the added benefit of double the half-life in blood plasma samples. The increase in half-life is due to CD-MOF-1 increasing the solubility of ibuprofen compared to the pure salt form.

(7) Semiconductors:

Workers proved that they can create electrically conductive thin films of MOFs ($Cu_3(BTC)_2$ (also known asHKUST-1; BTC, benzene-1,3,5-tricarboxylic acid) infiltrated with the molecule 7,7,8,8-tetracyanoquinododimethane) that could be used in applications including photovoltaics, sensors and electronic materials and a path towards creating semiconductors. The team demonstrated tunable, air-stable electrical conductivity with values as high as 7 siemens per meter, comparable to bronze. Ni (2,3,6,7,10,11-hexaiminotriphenylene)$_2$ was shown to be a metal-organic graphene analogue that has a natural band gap, making it a semiconductor, and is able to self-assemble. It represents a family of similar compounds. Because of the symmetry and geometry in 2,3,6,7,10,11-hexaiminotriphenylene (HITP), the overall organometallic complex has an almostfractal nature that allows it to perfectly self-organize. By contrast, graphene must be doped to give it the properties of a semiconductor. $Ni_3(HITP)_2$ pellets had a conductivity of 2 S/cm, a record for a metal-organic compound (Zhu and Xu, 2014)

(8) Bio-mimetic Mineralization:

Biomolecules can be incorporated during the MOF crystallization process. Biomolecules including proteins, DNA and antibodies could be encapsulated within ZIF-8. Enzymes encapsulated in this way were stable and active even after being exposed to harsh conditions (e.g. aggressive solvents and high temperature). ZIF-8, MIL-88A, HKUST-1, and several luminescent MOFs containing lanthanide metals were used for the biomimetic mineralization process.

(9) Carbon Capture:

Because of their small, tunable pore sizes and high void fractions, MOFs are a promising potential material for use as an adsorbent to capture CO_2. MOFs could provide a more efficient alternative to traditional amine solvent-based methods in CO_2 capture from coal-fired power plants (Choi *et al*., 2008 and Lian *et al*., 2016)

MOFs could be employed in each of the main three carbon capture configurations for coal-fired power plants: pre-combustion, post-combustion, and oxy-combustion. However, since the post-combustion configuration is the only one that can be retrofitted to existing plants, it garners the most interest and research. In post-combustion carbon capture, the flue gas from the power plant would be fed through a MOF in a packed-bed reactor setup. Flue gas is generally 40 to 60 °C with a partial pressure of CO_2 at 0.13 - 0.16 bar. CO_2 can bind to the MOF surface through either physisorption, which is caused by Van der Waals interactions, or chemisorption, which is caused by covalent bond formation. Once the MOF is saturated with CO_2, the CO_2 would be removed from the MOF through either a temperature swing or a pressure swing. This process is known as regeneration. In a temperature swing regeneration, the MOF would be heated until CO_2 desorbs. To achieve working capacities comparable to the amine process, the MOF must be heated to around 200 °C. In a pressure swing, the pressure would be decreased until CO_2 desorbs.

In addition to their tunable selectivities for different molecules, another property of MOFs that makes them a good candidate for carbon capture is their low heat capacities. Monoethanolamine (MEA) solutions, the leading method for capturing $CO_2$from flue gas, have a heat capacity between 3-4 J/g K since they are mostly water. This high heat capacity contributes to the energy penalty in the solvent regeneration step, i.e., when the adsorbed CO_2 is removed from the MEA solution. MOF-177, a MOF designed for CO_2 capture, has a heat capacity of 0.5 J/g K at ambient temperature.

(10) Desalination/ion Separation:

MOF membranes can mimic substantial ion selectivity. This offers the potential for use in desalination and water treatment. As of 2018 reverse osmosis supplied more than half of global desalination capacity, and the last stage of most water treatment processes. Osmosis does not use dehydration of ions, or selective ion transport in biological channels and it is not energy efficient. The mining industry, uses membrane-based processes to reduce water pollution, and to recover metals. MOFs could be used to extract metals such as lithium from seawater and waste streams. MOF membranes such as ZIF-8 and UiO-66 membranes with uniform subnanometer pores consisting of angstrom-scale windows and nanometer-scale cavities displayed ultrafast selective transport of alkali metal ions. The windows acted as ion selectivity filters for alkali metal ions, while the cavities functioned as pores for transport. The ZIF-8 and UiO-66 membranes showed a LiCl/RbCl selectivity of ~4.6 and ~1.8, respectively, much higher than the 0.6 to 0.8 selectivity in traditional membranes.

(11) Water Vapor Capture and Dehumidification:

A prototype has been developed that captures water vapor from the air, and then releases it with the application of a smaller amount of heat compared to existing commercially available technologies.

Such MOFs could also be used to increase energy efficiency in room temperature space cooling applications. Space cooling was responsible for approximately 3% of the 2016 total world primary energy use, and demand in developing countries is increasing at ever greater rates. Therefore, air conditioning efficiency is a very desirable area for reducing future increases in energy consumption and CO2 production from producing that energy (Czaja *et al*., 2009).

When cooling outdoor air, a cooling unit must deal with both the sensible heat and latent heat of the outdoor air. Typical vapor-compression-air-conditioning (VCAC) units manage the latent heat of the water vapor in air through cooling fins held below the dew point temperature of the moist air at the intake. These fins condense the water, dehydrating the air and thus reducing the heat content of the air substantially. Unfortunately, the energy usage of the cooler is highly dependent on the temperature of the cooling coil and would be improved greatly if the temperature of this coil could be raised above the dew point. This makes it desirable to handle dehumidification through means other than condensation. One such means is by adsorbing the water from the air into a desiccant coated onto the heat exchangers, using the waste heat exhausted from the unit to desorb the water from the sorbent and thus regenerate the desiccant for repeated usage. This is accomplished by having two condenser/evaporator units through which the flow of refrigerant can be reversed once the desiccant on the condenser is saturated, thus making the condenser the evaporator and vice-versa.

The conclusion is that a desiccant which can adsorb a large amount of water and then easily release that water would be ideal for this application. With MOFs' extremely high surface areas and porosities, they have been the subject of much research over the past decade in water adsorption applications.

(12) Ferroelectrics and Multiferroics:

Some MOFs also exhibit spontaneous electric polarization, which occurs due to the ordering of electric dipoles (polar linkers or guest molecules) below a certain phase transition temperature. If this long-range dipolar order can be controlled by the external electric field, a MOF is called ferroelectric. Some ferroelectric MOFs also exhibit magnetic ordering making them single structural phase multiferroics. This material property is highly interesting for construction of memory devices with high information density.The coupling mechanism of type-I $[(CH_3)_2NH_2]$ $[Ni(HCOO)_3]$ molecular multiferroic is spontaneous elastic strain mediated indirect coupling.

(13) MOF Nanocomposites for Biomedical Applications and Finding the Vaccines of COVID-19:

Scientists around the world are working on potential treatments and vaccines for the new coronavirus disease known as COVID-19. Several companies are working on antiviral drugs, some of which are already in use against other illnesses, to treat people who already have COVID-19. Other companies are working on vaccines that could be used as a preventive measure against the disease.With confirmed COVID-19 cases worldwide surpassing 3.5 million and continuing to grow, scientists are pushing forward with efforts to develop vaccines and treatments to slow the pandemic and lessen the disease's damage (Dolgopolovo *et al*., 2017). Some of the earliest treatments will likely be drugs that are already approved for other conditions ,or have been tested on other viruses "People are looking into whether existing antivirals might work or whether new drugs could be developed to try to tackle the virus," As of May, three medicationsTrusted Source had received emergency use authorization (EUA) from the Food and Drug Administration (FDA)-the anti-malaria drugs chloroquine and hydroxychloroquine, the anti-viral remdesivir, and a drug used to sedate people on a ventilator. An EUA allows doctors to use these drugs to treat people with COVID-19 even before the medications have gone through the formal FDA approval process. In mid-May, the small biotech company, Sorrento Therapeutics, announced it has an antibody drug that has been effective in early testing in blocking the virus that causes COVID-19. They say the drug could potentially be used to treat people with COVID-19 as well as help prevent infection.

When a MOF is combined with a polymer, its colloidal stability is enhanced without loss of crystalinity. However, a recurrent issue is the decrease of porosity due to the polymer obstructing the entrance to the pores, or the penetration of the polymer chains inside the MOF cavities. Besides increasing the stability, the polymer coating offers the possibility of adding targeting functionalities or introducing a stimuli-responsive release, allowing for the preparation of improved drug delivery or imaging devices. It has been demonstrated that the metal-organic-framework (MOF) based vaccines can be constructed by encapsulating ovalbumin (OVA) and attaching the cytosine-phosphate-guanine oligodeoxynucleotides (CpG ODNs) in/on zeolitic imidazolate framework-8 (ZIF-8) nanoparticles.

Up until now, the developed technologies for the use of polymer/MOF and BioMOF nanocomposites are limited due to the lack of knowledge surrounding the interactions of these materials with the human body. In our opinion, the future research efforts should focus, among other things, on the (bio)stability of these systems in physiological conditions and the long-term impact of such compounds on living organisms. Furthermore, since the use of therapeutic proteins is a very promising route in the development of specific drugs, focus should be given to the production of appropriate systems for the delivery of proteins without disrupting their bioavailability and activity. Other critical aspects include biocompatibility issues, batch-to-batch repeatability, pharmacokinetics/pharmacodynamics, dose response, clinical applications, etc. The pH responsive decomposition feature enables the system to release the protein antigens and CpG ODNs in the same antigen presenting cells more efficiently. More importantly, in addition to the induction of a potent immune memory response, both in vitro and in vivo experiments show that the vaccines can induce strong humoral and cellular immunity. These findings suggest that the MOF-based vaccine platforms can be used to produce effective vaccines against a range of ailments, which will facilitate the application of MOFs in biomedical areas.

CONCLUSION

In conclusion, polymer/MOF nanocomposites constitute a next generation class of multifunctional devices for biomedical applications that can greatly contribute to the improvement of personalized medicine and healthcare in general and COVID-19 in particular. These drugs are still being tested in clinical trials to see if they are effective against COVID-19. The step is needed to make sure the medications are safe for this particular use and what the proper dosage should be. Ayurvedic drugs like Ashwagandha, Aluveera gel are also supposed to be helpful as suggested by Baba Ramdev of Patanjali. Prof. Ranjana Kumari, Principal Katihar Engg. College Katihar in her official WhatsApp group shared about a homeopathic drug Arsenic Album-30 to be helpful in prevention of COVID-19.

So it could be months before treatments are available that are known to work against COVID-19. It could be even longer for a vaccine. But there are still other tools that can be used to reduce the damage done by the novel coronavirus. "Even though technological advances allow us to do certain things more quickly," "we still have to rely on social distancing, contact tracing, self-isolation, and other measures."

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