Review: Paramagnetic metal-organic framework composites and their applications

Rashmi R. Dubey, W. B. Gurnule,U. S. Purohit,S. G. Burade, S. S. Nagare.

[1]Department of Chemistry Kamla Nehru Mahavidyalaya, Nagpur -440024. MS, India

E-Mail: dube.rashmi.rd@gmail.com

ABSTRACT

Metal-organic framework (MOFs) is one of the interesting class of porous inorganic-organic hybrid networks synthesized from metal ions with multidentate organic ligands. Porous organic frameworks, such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), have been widely used in this research area because of their special features, and different methods have been developed and which makes MOFs promising materials for hazardous component removal from the environment. This review summarises the advantage of MOFs in the removal of hazardous contaminants from the environment. Different methods of synthesis of MOFs are also provided, in the final section we provide applications of MOFs.

Keywords: Keywords: metal organic framework, magnetite nanoparticles, encapsulation

INTRODUCTION:

MOFs are synthetic materials that emerged over the past three decades. They are comprising of organic ligands that bridge metal ions. This leads to highly ordered, porous and 3-dimensional crystalline structures. Paramagnetic metal organic frameworks are a class of material that contain both magnetic metal ions and organic ligands. These materials possess unpaired electrons that are localized on the metal ions, which makes them paramagnetic, they are attracted by an external magnetic field. The magnetic properties of these MOFs are unique and can be tuned by controlling the metal ions and ligand used in their synthesis.

These materials have potential applications in the areas including sensing, catalysis and data storage. Recently, multifunctional MOFs have attracted much attention as they involve diverse characters in one material, for instance, combining porosity with magnetism.[1]

Nanocomposites are hybrid materials that combine two or more different types of materials at the nanoscale level. Often resulting in properties unique to the composite materials. Paramagnetic MOFs can be incorporated into nanocomposites with other materials, such as polymers or nanoparticles, to increases their magnetic properties and improve their performance in various applications. These nanocomposites exhibit different implementation in sewage water purification, storage of hydrogen, gas – energy storage, conversion of CO_2, luminescent materials,biomedical imaging, solid phase extraction and antimicrobial agents. The metals used to make nanocomposites are chitosan, graphene, titanium, copper, gold, etc. The semi-conducting material also incorporated in the composites in order to acquire photocatalytic activity by electron-hole pair formation.

In addition to surface areas and porous nature, metal organic frameworks have storage mechanical strength and practically high thermal stability with considerable stability in harsh, toxic chemical atmosphere making them promising materials to meet the green chemistry standards. Titanium-based substances are widely used in various fields, such material is Ti2C3 used in energy storage, catalysis, and photochemical therapy due to hydrophilic functional group, strong redox reactivity, and more efficient electron transfer ability. TiO2 and g-C3N4 are formed to improve the shortcoming of MXenes by heterojunctions.[2]Amorphous silica nanoparticles comprise a class of widely used industrial nanomaterials, which may elicit acute inflammation in the lung. Lothar etal, studied paramagnetic Fe_2O_3/SiO_2 core/shell nanoparticles (Fe-Si-NP), These paramagnetic Fe-Si-NP appear well suited to study the binding of proteins to silica nanomaterials in the lung. [3]According to Lijin Huangetal, hollow covalent organic frameworks (COFs) have gained significant attention because of their specific properties, including enhanced surface-to-volume ratio, large surface area, hierarchical structure, highly ordered nanostructures, and excellent chemical stability. [4]The plant extracts,when added into nano-paramagnetic materials to form magnetic organic nanocomposites are more economical than other extracts and give good results. These plant extracts are generally proteins, sugars, terpenoids, polyphenols, alkaloids, and phenolic acids. These bioactive materials reduces metal ion into its nano structure [5] Silica aerogels are produced using sol–gel chemistry, due to this synthesis method, silica aerogels are highly nanoporous solid materials with a wide range of exceptional physical properties[6] T.S. Swathyetal,put forward a facile and green synthetic approach for the development of silver nanoparticles embedded polythiophene-functionalized multiwalled carbon nanotube nanocomposites by the reduction of silver nitrate with ascorbic acid (Vitamin-C) in aqueous medium [7]

Silver is most toxic to the pathogenic microorganism, very low toxic to the animal cell, and to be preferred against antibiotic-resistant bacteria as it is the highest form of antimicrobial element than any other element in the periodic table [8] Due to low cost, efficiency, high electrical conductivity, and thermal properties large number of polythiophene-functionalized multiwalled carbon nanotubeare prepared by injection of tangled silver [9]

Recently, the combination of Au, TiO_2, and CNT by self-assembly approaches has been studied. Zhang et al. reported a self-assembly method for synthesis of Au/TiO_2/CNT nanocomposite with the help of a photo assisted method to synthesize Au NPs on the surface of material previously prepared as support for TiO_2/CNT [10] A number of typical metal-oxide photocatalysts (ZnO, TiO2, MnO2, and CeO2) utilizing nanoscale morphology has been studied so far [11-16] The Au/TiO_2/CNT nanocomposite for the photocatalytic degradation of organic pollutant (methyl orange). However, these methods used organic solvent that reduced photocatalytic performance due to the presence of residual organic compounds [17]

Classification of Paramagnetic Nanoparticles

Lanthanides:

Lanthanides from the periodic table of elements such as gadolinium are among the most common and favourable paramagnetic materials because of possessing a high number of unpaired valence electrons.Lanthanides are promising and excellent T_1 shortening metals. The disadvantage of lanthanides is their high toxicity in their free form. But chelating lanthanide metal ions considerably decreases the toxicity level while supporting the practically high magnetic characteristic with applications as contrast agents in MRI.[18]

Manganese nanoparticles: The next class of nanoscale magnetic particles is manganese nanoparticles which have replaced gadolinium nanoparticles. Manganese has emerged as an alternative for gadolinium in treatment of patients with renal disorders as well as liver transplantation [19]

Iron oxide nanoparticles: Iron oxide nanoparticles, Fe_2O_3 and Fe_3O_4, are regarded as superparamagnetic agents with rapidly growing applications in separation science, tracking and cell labeling for the therapeutic purposes in cancer therapy, tumor ablation by hyperthermia and as diagnostic agents. Iron oxide nanoparticles applications depend on the tailored properties such as magnetism, surface chemistry, shape and size.[20]

Discussion and Applications:

Paramagnetism is a form of magnetism whereby some materials are weakly attracted by an applied magnetic field and form induced magnetic fields in the direction of the magnetic field and have have many applications for cancer diagnosis and therapy. More importantly, advances in nanoparticle engineering enable performance enhancements over molecular paramagnetic agents. A variety of paramagnetic materials and production methods enable the selection of nanoparticle size, shape, and surface chemistry, which are all important design parameters that determine a nanoparticle's diagnostic accuracy using magnetic resonance imaging, and therapeutic efficacy.Randall Toy etal, introduce ways in which paramagnetic nanoparticles may be used for targeted magnetic resonance imaging, for multimodal imaging, and as drivers for tumor therapy by hyperthermia and triggered drug release.[21] Pellico, Juan reported broad range of nanoparticulate MRI contrast agents hose associated with the paramagnetic ions Gd^{3+}, Mn^{2+}, Dy^{3+}, and Ho^{3+} as these shows striking MRI performance [22] Gadolinium oxides are the most utilised alternatives to Gd chelates, where it has been found that decreasing particle diameter results in a progressive trend towards higher relaxivities. Park et al. showed that the highest relaxivities were obtained for nanoparticles synthesised with an average diameter of d = 1–2.5 nm [23] Manganese monoxide nanocomposites functionalised with porous gold nanoclusters have also been used as pH-responsive probes. In this work, it was suggested that the gold nanoclusters sterically hinder the release Mn^{2+} from the particles, consequently providing delayed T1 contrast and a longer diagnostic window. They also allow the system to function as a multimodal probe with photoacoustic and X-ray CT imaging modalities additionally supported [24]

Photocatalytic TiO2 materials commonly used in AOP studies due to its overall cost, generation of reactive oxygen species, etc TiO_2 has large band gap of 3.2 eV to overcome this iO2 is modified to o increase the photocatalytic performance [25] The hyperjunction of carbon nitride (g-C3N4) and TiO_2 is used as a photocatalyst in the removal of NO, H_2 production, hydrocarbon oxidation, etc. the Frameworks optical and synergic electron transfer behaviour of g-C3N4 will enhance the optoelectronic behaviour of the TiO2 materials. Heterojunction nanocomposites absorbs light in the visible range.[26]

The g- C_3H_4 nanocompositeswhich have great stability and are easily available, but efficiency of work depend on metal in which hyperjunction is formed to increase its efficiency, nanorods are used. Figure:1 shows hydrogen evolution rate in gold and graphene combination in urea is four times greater than its combination with g-C_3H_4.[27]

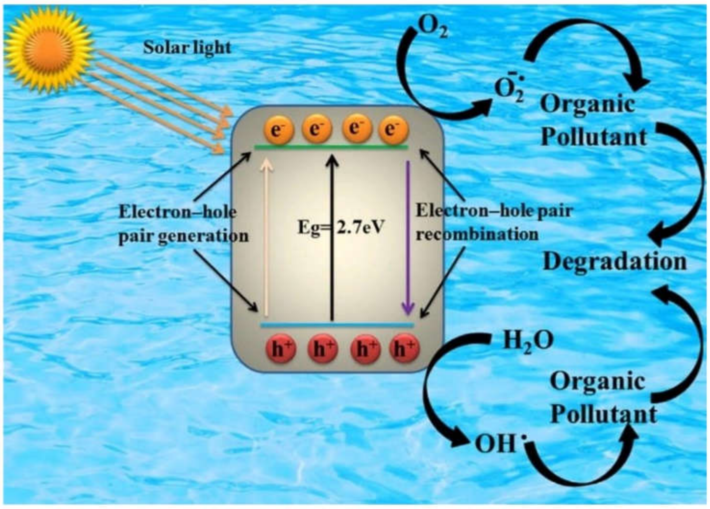

Figure 1: Metal free g-C3N4 photocatalyst for the degradation of organic pollutants present in water[28]

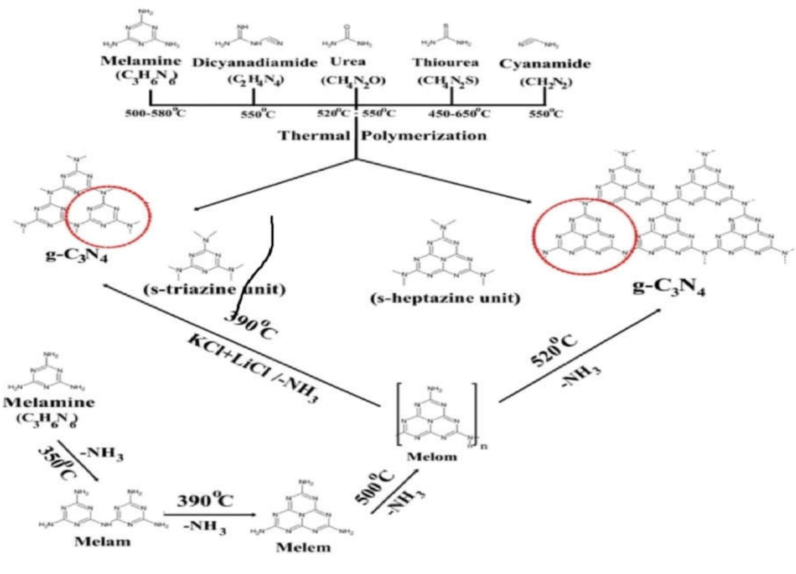

Figure 2: Fabrication of metal free g-C3N4 using different precursors.

The g-C3H4 is fabricated as in Figure:2, also has great application in food packaging to protect the shelf life of food. PVA is nontoxic biosynthetic polymer with excellent hydrophobic and film forming capacity its strength can be improved by adding fillers such as gold and graphene oxide nanoparticles [29]

The Organic -Inorganic paramagnetic nanocomposites shown in figurw:3, exhibit wide range of advantages. Binding of Organic materialon inorganic material enhances the biocompatibility. Some inorganic materials like Au,Ag,Co,Ni,Ru,Pt and Pd andmetal oxide Example of TiO2 into graphene (TiO2graphene) shows enhanced photocatalytic reaction in NOx reaction structures like CNT, graphene and some polymers. Example:TiO2 into graphene (TiO2graphene) shows enhanced photocatalytic reaction in NOx [30]

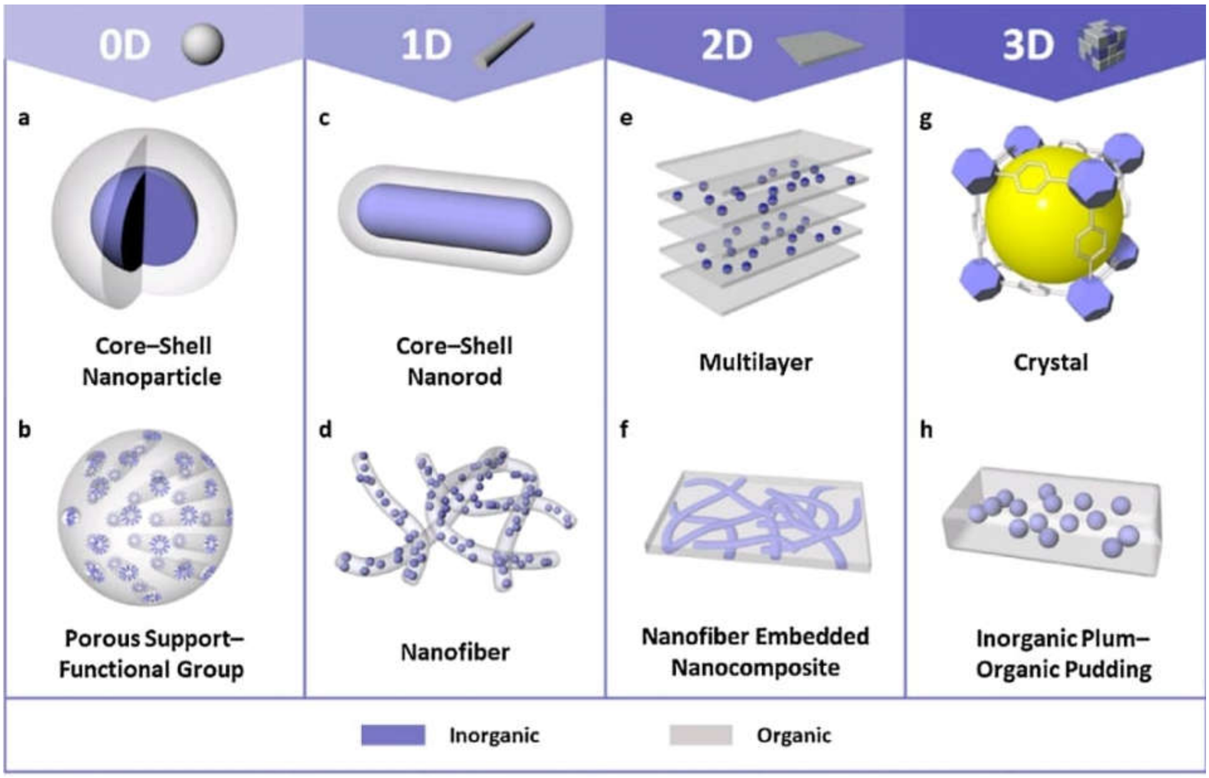

Figure 3: Various Structures of Nanocomposites

Lanthanides have been evaluated for their efficiency as T1 imaging agent. Liposomes and dendrimers are the primary nanostructure used to locate the to target sites [Figure:4] The gadolinium liposomes with targeted magnetic resonance imaging agent. To evaluate tumor angiogenesis and inflammation. Design of JD based agent requires knowledge of several factors because signal intensity is not linearly related to concentration of. Agent. To be emphasized that there will not be one size, shape and surface chemistry. That will optimize the performance of paramagnetic nanoparticles. All the three questions must be answered case by case to maximize the nanoparticles therapeutic performance.[32]

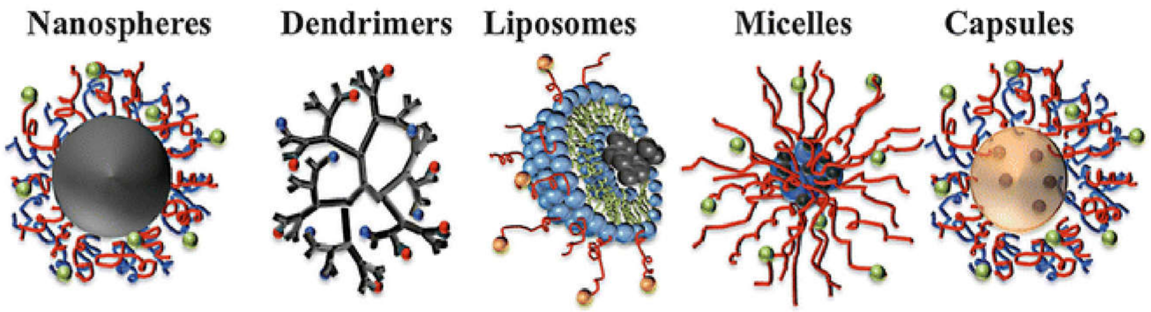

Figure 4: Common platforms for nanoparticles, incorporated into a variety of nanoparticle platforms, such as being entrapped in dendrimers, liposomes, or micelles, or loaded into capsules.[32]

Therapeutic applications of specific focus are tumor ablation via nanoparticle induced hyperthermia and triggered drug release through the magnetically induced mechanical disruption of nanoparticle composites that carry chemotherapy. Here is the summary of nanoparticle platform

Nanoparticle platform	Ligand type	Target	Reference
Iron oxide nanoparticles	Peptide	Integrins	[33]
		uPA receptor	[34]
		EDB	[35]
	Antibody	Chemokine Receptor	[36]
		VEGF	[37]
	Protein	Transferrin Receptor	[38]
Iron oxide nanochains	Peptide	Integrins	[39]
Capsules (iron oxide)	Peptide	Integrins	[40]
Lipid-based (gadolinium)	Peptide	Integrins	[41,42]
		Integrin/galectin-1	[43,44]
	Antibody	ICAM-1	[45]
		CD105	[46]
	Small molecule	FA Receptor	[47]
Perfluorocarbon nanoparticles	Various	Various	[48]
	Peptide	Integrins	[49]
	Antibody	Integrin	[50]
LipoCEST	Peptide	Integrin	[51]
Dendrimers (Gd)	Small molecule	FA Receptor	[52]

Conclusion:

Structure Science and technology is a broad and interdisciplinary area of research and development activity grown worldwide in the past decades. Nanocomposites have a very essential role among nanomaterials and can be synthesized by using simple and inexpensive techniques. this material has properties that are different as compared to conventional microscale composites during the last decades, the development of paramagnetic MOFs has been the source of Discovery with potential applications in the field of information technology, telecommunication, or medicines. The important magnetic property of nanomaterial is applicable in CMR and other therapeutic uses. Incorporation of nanoparticles with different platforms like in dendrimers, liposomes, or micelles, or loaded into capsules have great importance in therapeutic use for tumor ablation.

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