Coordination Polymers, Its Properties and Application: A Review

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Abstract: Coordination polymers (CPs) represent a fascinating class of crystalline materials formed by the coordination of metal ions or clusters with multidentate organic ligands, resulting in extended one-, two-, or three-dimensional frameworks. Their unique structural versatility and tunable properties have attracted significant attention in materials science, chemistry, and related disciplines. This review focuses on the synthesis strategies, structural diversity, and physicochemical properties of coordination polymers, including porosity, thermal stability, optical behavior, and magnetic characteristics. The discussion further highlights the wide range of applications of CPs in areas such as gas storage and separation, catalysis, drug delivery, sensing, and environmental remediation. Special emphasis is placed on recent advancements in designing CPs with tailored functionalities to address energy and environmental challenges. The review concludes with an outlook on the future prospects and challenges in the development of multifunctional coordination polymers for advanced technological applications.

Keywords: Coordination polymers (CPs), Metal organic frameworks (MOFs), Catalyst, Gas storage, Hydrothermal.

1. INTRODUCTION

Coordination polymers (CPs) are a fascinating class of crystalline materials that have captured significant interest in modern materials science due to their structural diversity, tunable properties, and wide range of applications. A coordination polymer is defined as a network structure in which metal ions or metal clusters act as nodes and are linked together by organic or inorganic ligands through coordination bonds, extending the structure into one-, two-, or three-dimensional frameworks. When these frameworks exhibit permanent porosity, they are often referred to as metal-organic frameworks (MOFs), which are one of the most studied subclasses of CPs. The ability to systematically design and synthesize CPs with desired structural and functional characteristics has positioned them as promising materials for applications ranging from gas storage and catalysis to drug delivery and environmental remediation. The concept of coordination chemistry was first established in the late 19th century by Alfred Werner, whose pioneering work earned him the Nobel Prize in Chemistry in 1913. Werner's discoveries on the bonding and geometry of coordination complexes laid the foundation for the modern understanding of coordination polymers. However, the development of CPs as advanced functional materials only began to accelerate during the 1990s, when breakthroughs in synthetic methods and characterization techniques enabled chemists to design extended coordination networks with predictable topologies and properties. The landmark synthesis of MOF-5 by Yaghi and co-workers in 1999 demonstrated the immense potential of CPs as highly porous materials with record-breaking surface areas, sparking an explosion of research interest in this field. Despite the remarkable progress in the field of CPs, certain challenges remain. Scaling up the production of CPs while maintaining their structural integrity and porosity is a major hurdle for industrial applications. The stability of CPs under real-world conditions, such as humid or acidic environments, also needs improvement. Additionally, while many CPs show excellent performance in laboratory conditions, their long-term durability and cost-effectiveness in practical applications require further evaluation. Future research is expected to focus on designing stimuli-responsive CPs that can change their properties in response to external triggers such as temperature, light, or electric fields. Another promising direction is the integration of CPs with other materials, such as polymers, nanoparticles, or graphene, to create hybrid composites with enhanced mechanical and functional properties. Advances in computational modeling, machine learning, and high-throughput screening are also accelerating the discovery of new CPs with targeted functionalities [1-4].

2. SYNTHESIS STRATEGIES

Several synthetic strategies have been developed for the preparation of coordination polymers, each offering control over the size, crystallinity, and morphology of the final product [5]:

2.1. Solvothermal and Hydrothermal Synthesis:

This is one of the most common techniques used to synthesize CPs. It involves dissolving metal salts and organic linkers in a solvent (or water for hydrothermal) and heating the mixture in an autoclave under controlled temperature and pressure. The slow crystallization under these conditions often yields highly crystalline CPs.

2.2. Layer-by-Layer (LbL) Assembly:

This method is particularly useful for fabricating thin films of CPs. Metal ions and organic linkers are alternately deposited on a substrate, allowing precise control over film thickness and orientation.

2.3. Microwave-Assisted Synthesis:

Microwave irradiation accelerates the reaction kinetics, leading to faster synthesis and improved crystallinity. This technique is also energy-efficient and suitable for scaling up production.

2.4. Mechanochemical Synthesis:

In this solvent-free method, mechanical grinding of metal salts and organic ligands induces the formation of coordination bonds. It is an environmentally friendly approach that aligns with the principles of green chemistry.

2.5. Post-Synthetic Modification (PSM):

After the initial formation of a CP, additional functional groups or active sites can be introduced through chemical modification, enhancing its functionality without altering the overall framework structure.

The choice of synthesis method often depends on the desired properties and applications of the CP. Factors such as solvent, temperature, pH, and reaction time play critical roles in determining the final structure and porosity of the material.

3. PROPERTIES OF COORDINATION POLYMERS

The distinctive properties of coordination polymers (CPs) stem from their hybrid framework, which integrates inorganic metal centers with organic ligands. By carefully choosing the building blocks and optimizing synthetic conditions, these properties can be tailored, rendering CPs highly versatile and functional materials. The major properties of CPs are outlined below [6]:

3.1. Structural diversity and tenability:

Coordination polymers (CPs) exhibit remarkable structural diversity and tunability due to the infinite possibilities of combining metal ions or clusters with organic or inorganic ligands. The structure of CPs can range from one-dimensional (1D) chains and two-dimensional (2D) sheets to three-dimensional (3D) frameworks, depending on the coordination geometry of the metal nodes and the design of the linkers. This diversity allows the creation of frameworks with varied topologies, such as cubic, hexagonal, or zeolitic structures, which can be tailored to achieve specific pore sizes, shapes, and functionalities. Tunability is achieved through careful selection of building blocks, functionalization of ligands with chemical groups (e.g., $–NH_2$, $–OH$, $–SO_3H$), and incorporation of mixed metals or mixed linkers, which modify the physical and chemical properties of the framework. Furthermore, post-synthetic modification (PSM) techniques enable the addition of functional groups or guest molecules after the CP is formed, allowing for fine control over surface chemistry, adsorption selectivity, and catalytic performance. This combination of structural diversity and tunability makes CPs versatile materials for applications such as gas storage, catalysis, sensing, and environmental remediation.

3.2 Luminescence properties:

The luminescence properties of coordination polymers (CPs) arise from the synergistic interaction between metal centers and organic ligands, making them promising materials for optical and sensing applications. Luminescence in CPs can originate from various mechanisms, including ligand-centered emission, metal-centered transitions, ligand-to-metal charge transfer (LMCT), or metal-to-ligand charge transfer (MLCT). Incorporating luminescent metal ions, such as lanthanides (e.g., Eu^{3+}, Tb^{3+}), or chromophoric ligands enhances their ability to emit strong and tunable light. The emission wavelength, intensity, and lifetime can be precisely adjusted by modifying the coordination environment, ligand functionalization, or introducing guest molecules within the framework. This tunability makes CPs effective as chemical sensors, where the emission can change upon interaction with specific analytes like metal ions, gases, or explosives. Moreover, their high thermal and chemical stability ensures reliable performance in photonic devices, light-emitting diodes (LEDs), and bio-imaging applications.

3.3. Magnetic properties of coordination polymers:

The magnetic properties of coordination polymers (CPs) arise from the presence of paramagnetic metal ions and the way they are connected through bridging ligands, which mediate magnetic exchange interactions. Transition metals such as Mn^{2+}, $Fe^{2+}/^{3+}$, Co^{2+}, and Ni^{2+}, as well as lanthanides with unpaired d- or f-electrons, are commonly incorporated into CP frameworks to impart magnetism. Depending on the metal-ligand arrangement and the type of interactions (ferromagnetic or antiferromagnetic), CPs can exhibit a wide range of magnetic behaviors. Some CPs also display advanced phenomena like single-molecule magnetism (SMM), where individual molecules retain magnetic memory, or spin-crossover (SCO), where the spin state of the metal center switches in response to external stimuli such as temperature, light, or pressure. The magnetic properties of CPs can be fine-tuned by altering the metal nodes, the electronic nature of the ligands, or the framework topology, making them attractive for applications in data storage, molecular spintronics, quantum computing, and magnetic sensing technologies.

3.4. Porosity and high surface area:

The porosity and high surface area of coordination polymers (CPs), particularly metal-organic frameworks (MOFs), are among their most distinctive and valuable properties. CPs possess well-defined channels, cages, and voids within their crystalline structures, resulting from the periodic arrangement of metal nodes and organic linkers. These pores provide exceptionally high internal surface areas, often exceeding 5000 m^2/g, which surpass those of conventional porous materials such as zeolites or activated carbons. The pore size, shape, and surface chemistry of CPs can be precisely tuned by selecting appropriate ligands, metal ions, or by employing post-synthetic modification techniques. This tunability allows for selective adsorption of gases or molecules, making CPs highly effective for applications in gas storage (e.g., hydrogen, methane), carbon dioxide capture, and molecular separation. Furthermore, the open-framework design and large surface area enhance their catalytic activity and adsorption capacity, enabling efficient interactions with guest molecules.

3.5 Conductivity:

The conductivity of coordination polymers (CPs) arises from the ability of their frameworks to facilitate charge or ion transport through extended metal-ligand networks. While most CPs are traditionally insulating due to the localized nature of their electronic states, conductivity can be introduced or enhanced by incorporating π-conjugated organic ligands, mixed-valence metal centers, or redox-active components that enable efficient electron delocalization. Conductive CPs and MOFs often rely on pathways formed by metal–ligand overlap or guest molecules (e.g., iodine, TCNQ) that act as charge carriers. Depending on the design, CPs can exhibit metallic, semiconducting, or ionic conductivity, making them suitable for applications in sensors, supercapacitors, batteries, fuel cells, and electrocatalysis. The conductivity can be tuned by modifying the framework structure, doping, or introducing conductive polymers and nanoparticles into the pores. Recent advancements have produced CPs with notable electrical conductivities comparable to traditional conductive materials, while retaining the porosity and tunability unique to CPs.

3.6. Catalytic properties:

Coordination polymers (CPs), especially metal-organic frameworks (MOFs), display remarkable catalytic properties due to their unique structural features, including the presence of metal ions or clusters that serve as active sites and organic ligands that provide functional groups and structural flexibility. The coordinatively unsaturated metal sites within CP frameworks can activate reactant molecules, enabling a wide variety of chemical transformations. Their high surface area and well-defined porosity ensure easy diffusion and accessibility of reactants and products, resulting in enhanced catalytic performance. The catalytic behavior of CPs can be precisely tuned by selecting appropriate metal centers (e.g., Cu, Fe, Co, or Zn) and functional ligands with desired chemical properties (e.g., $–NH_2$, $–COOH$, $–SO_3H$ for acid/base catalysis). For instance, MOF-74 with open metal sites has been extensively used in gasphase reactions, while MIL-101 and UiO-66 have shown high efficiency in oxidation, hydrogenation, and condensation reactions. Furthermore, CPs have gained attention in photocatalysis and electrocatalysis, where their ability to stabilize reactive intermediates makes them ideal for energy conversion and environmental applications. Through post-synthetic modification (PSM), additional catalytic species such as metal nanoparticles, enzymes, or functional groups can be incorporated into CP frameworks, further enhancing their catalytic versatility. Owing to their reusability, structural robustness, and hybrid nature, CPs serve as an excellent bridge between homogeneous and heterogeneous catalysts, offering immense potential in industrial processes, energy applications, and pollution control.

3.7. Thermal and chemical stability:

The thermal and chemical stability of coordination polymers (CPs) is a crucial factor determining their practical applications in harsh industrial and environmental conditions. Stability largely depends on the strength of the metal-ligand coordination bonds, the topology of the framework, and the nature of the organic linkers. Early generations of CPs were often unstable when exposed to moisture, acids, or high temperatures; however, modern CPs, particularly certain metal-organic frameworks (MOFs) like ZIF-8, UiO-66, and MIL-101, exhibit excellent thermal stability (often up to 500 °C) and remarkable resistance to water, acids, and organic solvents. The robustness of these frameworks can be further enhanced by using high-valent metal clusters (e.g., Zr^{4+}, Al^{3+}, Cr^{3+}) and rigid linkers that form strong coordination bonds. Post-synthetic modifications and surface functionalizations can also improve chemical resistance, allowing CPs to retain their crystallinity and porosity under extreme conditions. This high stability makes CPs ideal for applications such as gas storage, catalysis, sensing, and environmental remediation, where durability and resistance to degradation are essential.

4. APPLICATION OF COORDINATION POLYMERS

Coordination polymers (CPs), especially metal-organic frameworks (MOFs), are widely utilized owing to their exceptional combination of adjustable structures, large surface areas, intrinsic porosity, and versatile functionalities. The hybrid architecture of CPs, formed by the coordination of metal centers with organic linkers, enables fine-tuning of their properties to suit diverse requirements across industrial, environmental, and biomedical applications. The major applications of CPs include [7-11]:

4.1. Catalysis:

Coordination polymers (CPs), particularly metal-organic frameworks (MOFs), have emerged as highly efficient heterogeneous catalysts due to their large surface area, tunable pore structure, and the presence of active metal sites. The metal ions or clusters within CPs act as catalytic centers, while the organic linkers provide functional groups that can participate in or enhance catalytic reactions. The porous framework of CPs ensures easy diffusion of reactants and products, improving reaction efficiency compared to traditional catalysts. By selecting specific metal nodes (e.g., Cu, Fe, Zr, or Co) and functionalized ligands (e.g., $–NH_2$, $–SO_3H$, –COOH), CPs can be tailored for a wide range of catalytic processes such as oxidation, hydrogenation, esterification, C–C coupling, and photocatalysis. For instance, UiO-66 and MIL-101 have shown remarkable performance in oxidation and condensation reactions due to their strong Lewis acid sites and high stability. Moreover, CPs are ideal for photocatalysis and electrocatalysis, where their framework can efficiently absorb light or facilitate electron transfer. Post-synthetic modification (PSM) allows the incorporation of additional catalytic species like metal nanoparticles or enzymes, further enhancing their catalytic activity. The reusability, structural stability, and hybrid nature of CPs make them attractive alternatives to conventional catalysts in industrial processes, energy conversion, and environmental remediation.

4.2. Gas Storage and Separation:

CPs with high porosity and large surface areas are excellent materials for storing gases such as hydrogen, methane, and carbon dioxide. CPs can differentiate gases based on molecular size and polarity (e.g., separating CO_2 from CH_4 or N_2) by adjusting the pore size and urface chemistry of the framework. MOFs are used to purify natural gas by removing CO_2 and H_2S, which improves fuel quality. Certain CPs can separate O_2 from N_2 due to their selective adsorption characteristics, which is vital for medical and industrial oxygen generation.

4.3 Drug Delivery and Biomedical Applications

Biocompatible CPs constructed from non-toxic metals like Zn or Fe, and biodegradable linkers, are used as drug carriers. Their tunable pore sizes allow the encapsulation of therapeutic agents, while their stimuli-responsive behavior ensures controlled release. CPs are also explored for bioimaging and as antibacterial agents.

4.4. Sensing

CPs exhibit luminescent and electrochemical sensing properties due to changes in their emission or conductivity upon interaction with analytes. They are effective for detecting toxic gases, explosives, heavy metals, and organic pollutants at low concentrations. For example, Eu^{3+}-based MOFs are widely used as fluorescence sensors for nitroaromatic compounds.

4.5. Environmental Remediation

CPs serve as effective adsorbents for removing pollutants, such as heavy metals (e.g., Pb^{2+}, Hg^{2+}), dyes, and toxic organic compounds from water and air. Their regenerability and high removal capacity make them highly suitable for water treatment and environmental protection.

4.6. Energy Storage and Conversion:

Conductive CPs and MOF-based composites are increasingly being used in batteries, supercapacitors, and fuel cells. They enhance energy storage performance due to their high surface area, conductivity (after modification), and redox-active sites.

4.7. Magnetic and Electronic Applications

Coordination polymers (CPs) exhibit significant magnetic and electronic applications due to the presence of metal ions with unpaired electrons and the conjugated organic linkers that facilitate electron delocalization. In magnetic applications, CPs can behave as single-molecule magnets, spin-crossover materials, or magnetic conductors, making them useful in high-density data storage, quantum computing, and spintronic devices. The ability to tune the metal centers and bridging ligands allows precise control over magnetic interactions, such as ferromagnetism or antiferromagnetism. In electronic applications, CPs and MOFs with π-conjugated linkers and redox-active metal centers can exhibit semiconducting, conducting, or even superconducting behavior. These properties make them potential materials for sensors, energy conversion devices, batteries, and field-effect transistors. The combination of structural flexibility and functional tunability enables CPs to integrate magnetic and electronic properties, opening avenues for multifunctional advanced materials.

5. CONCLUSION

Coordination polymers (CPs), especially metal-organic frameworks (MOFs), form a highly versatile class of hybrid materials characterized by exceptional structural diversity and tunable properties. Their key attributes, including high porosity, large surface area, thermal and chemical stability, and functional adaptability, make them ideal for diverse applications. CPs have shown outstanding potential in areas such as gas storage and separation, catalysis, sensing, drug delivery, and the development of magnetic and electronic devices. The ability to finely tune metal nodes and organic linkers enables the creation of materials with precisely tailored functionalities. Ongoing research in their synthesis and modification is expected to further enhance their performance and unlock new opportunities in energy, environmental sustainability, and advanced technological innovations.

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