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Review

# Recent advances on polyoxometalates intercalated layered double hydroxides: From synthetic approaches to functional material applications

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ABSTRACT

Polyoxometalates (POMs) exhibit attractive properties and great potential to meet with contemporary society demands regarding environment, materials, energy, health and information technologies, etc. The development of POM-based advanced functional materials is of significance to effectively utilize POMs in meeting various challenges. In recent years, the intercalation of POM anions into layered double hydroxides (LDHs) has been a versatile and important approach for the development of POM-based multifunctional materials. The current review summarizes the latest progress on the preparation of POM intercalated LDHs (denoted as POM/LDHs) and their material application.

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## 1. Introduction

Polyoxometalates (POMs) are a class of discrete anionic metal oxides of groups 5 and 6 and POMs exhibit attractive properties such as thermal and oxidative stability, remarkable electronic and magnetic properties, and Brønsted acidity, etc., which result in intriguing applications ranging from medicine, catalysis to

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material science. We have witnessed significant progress during past decades that have been summarized in different books, reviews and thematic journal issues [1–10], including books by Pope and Müller [1,2], a review by Pope and Müller [3], the thematic POM issues in Chemical Reviews and in Chemical Society Reviews [4,5], and several contributions from Coordination Chemistry Reviews [6–10].

POMs are most well-known as catalysts and have been widely applied in industry [11–14]. The development of highly efficient, easily recovered and reusable POM-based heterogeneous catalysts has long been and will continue to be the focus for the practical application of POMs. As a result, two strategies [15–19], namely "solidification" and "immobilization" of catalytically active POMs, have been adopted in the development of POM-based molecular heterogeneous catalysts. One way for the immobilization of POMs is the intercalation of POMs into LDH layers, which results in the formation of a number of interesting nanocomposites with unique properties.

The first scientific publication of the POM/LDH nanocomposites was reported by Pinnavaia [20]. It should be mentioned that an interesting POM/LDH composite material was reported to be able to apply in exhaust gas and hydrocarbon conversion in a US patent [21]. The POM/LDH nanocomposites are a class of very important and versatile materials. Previously, Wang et al. [22], Pinnavaia et al. [23], Rives and Ulibarri [24], Hu and Li [15], and Rives et al. [16] reviewed this type of materials from different perspective, and most of them mainly focused on the introduction of the preparation methods, characterization and some application in catalytic reactions. In this review, after brief introduction of the classical synthetic approaches (ion exchange, reconstitution, and co-precipitation) of the POM/LDH nanocomposites, we summarize some other synthetic pathways that have been employed in engineering the POM/LDH composite materials in recent years. The important applications of the POM/LDH nanocomposites in material science have been highlighted and discussed.

## 2. Synthesis of the POM/LDH nanocomposites

### 2.1. Polyoxometalates (POMs)

POMs are built from condensation of metal oxide polyhedra ($MO_x$, M = $W^{VI}$, $Mo^{VI}$, $V^V$, $Nb^V$, $Ta^V$, etc., and $x$ = 4–7) with each other through corner-, edge-, or rarely in a face-sharing manner [11–13,25–28]. The metal atoms are referred to as addenda atoms. The atoms that can function as addenda are those that can change their coordination with oxygen from 4 to 6 as the $MO_x$ polyhedra condense in solution upon acidification [27,28]. Although oxygen is the ligand that mostly coordinates with the addenda atoms, other atoms/groups such as sulphur, bromine, nitrosyl and alkoxy, have been substituted in some of the POM clusters reported [29,30].

When the POM framework exclusively contains addenda metals (from groups 5 and/or 6) and oxygen, the cluster is called isopolymetalate, and the Lindqvist type anion $[M_6O_{19}]^{2-}$ is an archetypical example (Fig. 1). When the POM shows additional elements besides addenda metals and oxygen, it is known as a heteropoly complex, which is formed by condensation of $MO_x$ polyhedra around a central heteroatom as the solution is acidified [27,28]. Many different elements can act as heteroatoms in the heteropoly complex with various coordination numbers: 4-coordinate (tetrahedral) in Keggin and Wells-Dawson structures (e.g., $PO_4^{3-}$, $SiO_4^{4-}$, $AsO_4^{3-}$); 6-coordinate (octahedral) in Anderson-Evans structure (e.g., $Al(OH)_6^{3-}$, $TeO_6^{6-}$); 12-coordinate (Silverton) in $[(UO_{12})Mo_{12}O_{30}]^{8-}$. See Fig. 1 for some common POM structures in polyhedra representations.

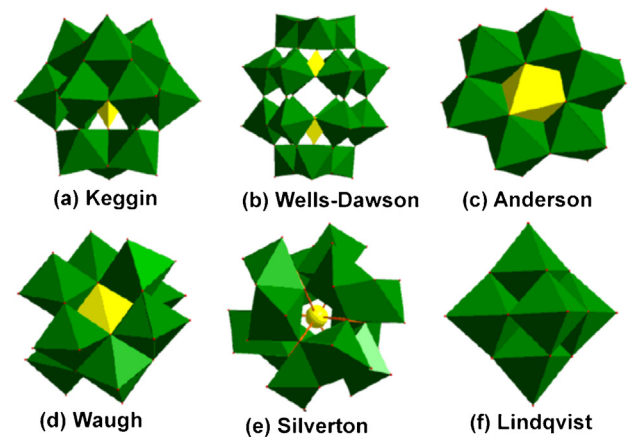


**Fig. 1.** Classical POM structures in polyhedral representations.

### 2.2. Layered double hydroxides (LDHs)

LDHs comprise an unusual class of layered materials with positively charged nanosheets/layers and the balancing anions located in the interlayer region. LDHs consist of a broad range of compositions of the type: $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}(A^{n-}{}_{x/n})\cdot zH_2O$; where $M^{2+}$ and $M^{3+}$ metal ions occupy octahedral positions in the hydroxide layers, $A^{n-}$ is the gallery anion, $x$ = 0.17–0.33 and it is defined as the $M^{3+}/(M^{2+} + M^{3+})$ ratio [31,32]. The interlayer anions are linked with positively charged host layer by means of electrostatic force and hydrogen bonding interactions through the water molecule of the interlayer or the hydroxyl group on the sheets (Fig. 2) [33,34]. In contrast to LDHs, most other layered materials have negatively charged sheets with charge-balancing cations in hydrated interlayer regions, such as phylosilicate clays and zirconium phosphates, etc. [35–38].

LDHs have been known for more than 150 years since the discovery of the mineral hydrotalcite, $[Mg_6Al_2(OH)_{16}]CO_3\cdot 4H_2O$ [24]. Partial substitution of the $Mg^{2+}$ ions by the $Al^{3+}$ ions in hydrotalcite compositions leads to the formation of positively charged

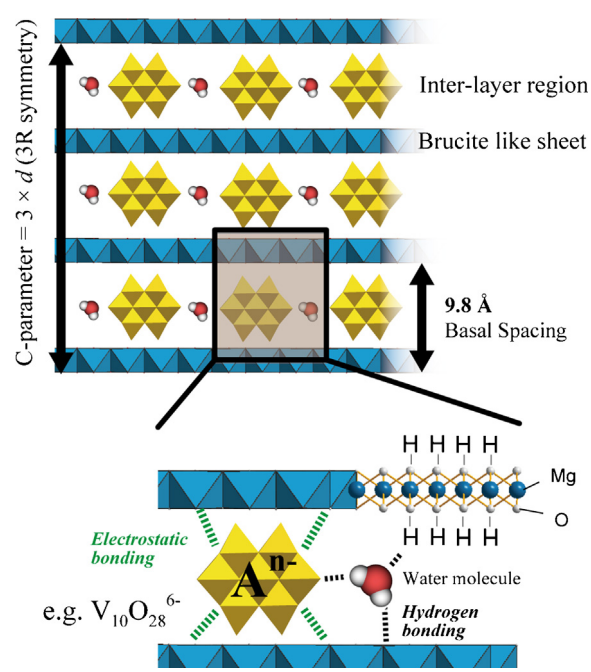


**Fig. 2.** Schematic representation of the $V_{10}O_{28}$/LDHs structure ($H_2O$ molecules in the interlayer: spacefill style) [24].

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