A review on functional nanoarchitectonics nanocomposites based on octahedral metal atom clusters (Nb₆, Mo₆, Ta₆, W₆, Re₆): inorganic 0D and 2D powders and films

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1. Introduction

Today, the term 'nanocomposite', proposed by Blumstein in 1961 [1], describes generally a bi(or multi)phasic material where one of the phases, at least, presents a nanometric size. The definition and the choice of materials are very broad including metallic, ceramic or polymer compounds [2–4]. Indeed, the high flexibility of the composition and the complexity of the structure have allowed various kinds of nanocomposites to be developed, zero-dimensional (0D)
(e.g. nanoparticles), one-dimensional (1D) (e.g. nanowires), two-dimensional (2D) (e.g. multilayered-based film and coating composites), three-dimensional (3D) (e.g. mesoporous-based composites) and the even more complex hierarchical 3D nanostructured networks [5]. In this review, this term will refer only to functional composite nanoarchitectures, which represent a class of nanostructured entities that integrate dissimilar nanoscale inorganic octahedral metal cluster units in the frame of the nanoarchitectonics concept [6–11]. As one of the nanocomponents of the nanocomposites, the nanometer-sized metal atom clusters (MC) also called ‘nanoclusters or superatoms’ (size <2 nm) [12], which consist of less than a few dozens of metal atoms, were used to synthesize functional nanocomposites during the last decades. Indeed, metal nanoclusters are promising candidates for novel materials due to their size-specific properties arising from unique atomic packing and electronic structures. Most of the papers are dedicated to silver, platinum and gold nanoclusters for catalysis, optics, sensors or biotechnology [13–28]. In parallel to this commonly studied family of nanoclusters, nanocomposites based on molecular octahedral metal atom clusters (Nb, Mo, Ta, W, Re) units were developed more recently. [See reviews [29–36] Although less popular than noble metal nanoclusters or superatoms, these octahedral transition metal atom clusters, with general formulas \( \{M\}_{6}L_{12}L_{6}^{\text{inner+/-}} \) or \( \{M\}_{6}L_{12}L_{6}^{\text{outer+/-}} \), are well known for one century and are a part of the large family of the transition metal atom nanocluster compounds defined by Cotton [37]. The \( \{M_{6}\}_{6}L_{6}^{\text{inner+/-}} \) nanosized cluster units are generally built up from an octahedral \( M_{6} \) clusters with Mo, W or Re metals, whereas the \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{outer+/-}} \) are based mainly on Nb or Ta metals [38–41]. These \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{outer+/-}} \) and \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{inner+/-}} \) cluster units are bonded to eight inner face-capping ligands or twelve face-capping ligands (L\(^{i}\), i = inner, L = Cl, Br, I, S, or Se), respectively, and both of them have six apical ligands (L\(^{a}\), a = apical, L = F, Cl, Br, I, OH, CN, organic molecules, and so on) located in terminal positions. These species can be isolated (at molecular level) or condensed by either ligands or metals in the solid-state compounds [39–41]. Depending on the degree of condensation and dimensionality of the metal atom clusters, these compounds present fascinating crystal structures and electronic properties as, for instance, superconductivity [42], thermoelectricity [43], intercalation/de-intercalation [44] or Mott insulating behaviors [45]. This review will focus only on molecular cluster compounds, in which cluster units are fully isolated in the crystal structures. For illustration, the molecular \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{inner+/-}} \) (M = Mo, W, Re) and \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{outer+/-}} \) (M = Nb, Ta) cluster units are represented in Figure 1.

These molecular metal atom cluster units can be defined as a link between atom and nanoparticle. The solid-state compounds built-up from these units are characterized by insulating behavior combined with specific physical and chemical properties. Generally, the molecular compounds based on non-interacting face-capped \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{inner+/-}} \) cluster units (M = Mo, W, Re; \( L^{i} \) = halogen; \( L^{a} \) = halogen, organic molecules) are characterized by strong phosphorescence that ranges from red to near-IR (NIR) with a high quantum yield and long lifetime [44–52], whereas, the molecular compounds based on non-interacting edge-bridged \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{outer+/-}} \) cluster units (M = Nb and Ta; \( L^{i} \) = halogen) are well known to be strong ultraviolet (UV) and NIR absorbers [53,54]. Several parameters influence the general properties of the cluster units: the nature of the metal, the nature of the ligands and the number of electrons involved in the metal – metal bonds, the so-called valence electron count or concentration (VEC). This review is not dedicated to the synthesis and properties of the octahedral metal atom clusters, for more specific details see these references [39,40,55–67]. These cluster units are prepared either by solid-state chemistry or by combined use of solid state and solution chemistries and associated with inorganic or organic counter cations in a large variety of molecular metal atom cluster compounds [37–67]. Actually, although prepared by solid-state chemistry processes, for instance, the \( \text{Cs}_{2}\{\text{MoBr}_{8}\}_{6} \) clustered compounds can be resolubilized in many solvents until obtaining 1 nm objects in solution thanks to their molecular properties [68]. Indeed, one of the key points is the high solubilization of these molecular metal atom clusters compounds in various solvents and matrices, which was an important parameter to provide very interesting building blocks with multifunctional properties (optical, magnetic, electronic, redox, and so on) that can be further used for the design of a large variety, from hybrids (dendrimers, liquid crystals, polymers, and so on) to all-inorganic, of functional nanocomposite materials and surface coatings during the last decades [29–36, 68–219].

Figure 1. Schematic representation of \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{outer+/-}} \) (M = Nb, Ta) and \( \{M_{6}L_{12}\}_{6}L_{6}^{\text{inner+/-}} \) (M = Mo, W, Re) molecular cluster units. Apical ligands (L\(^{a}\)) and inner ligands (L\(^{i}\)).
Clearly, the number of publications about nanocomposites based on octahedral metal atom clusters has been increasing for the last 3 decades (started from less than 10 before 2000 to almost 100 between 2010 and 2019, and already 43 since the last two years). These nanocomposites based on these octahedral nanoclusters are already an emerging field in material science. They found applications in many important domains like energy [91–108], catalysis [94,109–119,217], biotechnology [47,120–145], sensors [75,80,142,146–153], and photonic (Figure 2) [89,154–171].

Due to the remarkable properties of these octahedral metal atom clusters, a large number of studies are reported and this article will review only the inorganic powder (nanoparticles, 2D) and film nanocomposites. More specifically, the relationships between synthesis, properties and process of these inorganic powders and film nanocomposites will be discussed and new trends will be emphasized:

The electrophoretic deposition (EPD) process appears to be a new strategy to fabricate highly transparent, homogeneous and colored nanocomposite thin films and coatings,

The clear potential of Mo₆-based nanocomposites for biotechnology applications as antibacterial or anti-cancer or as a new broadband emitter for photovoltaic (PV), photonic and sensor applications,

The strong potential and synergetic effects of nanocomposites based on nanoclusters and layered 2D compounds for catalysis and photocatalysis applications,

The reborn of Nb₆ and Ta₆ nanoclusters, which appeared recently as very interesting UV and NIR blockers for saving energy applications.

One of the objectives of this review would be to provide guiding significance for design of new high-performance nanocomposites based on transition metal atom clusters from the aspects of processing, characterization and applications.

2. Inorganic powder nanocomposites: 0D nanoparticles and layered materials

The idea of improving the properties of materials by combining at least two phases with different properties is not new and nanocomposites are found in nature or have been created by human long time ago [220]. As mentioned in the introduction, the diversity of the architectures to prepare nanocomposites is very large. Nevertheless, in the case of inorganic nanoparticles (0D) and layered (2D) material nanocomposites, the nanoclusters are mainly embedded into nanoparticles (often considered as the matrix) or deposited at the surface of nanocrystals or nanoparticles or 2D materials, depending on the targeted application. The

![Figure 2](image-url). The illustration of the applications in $[\text{Mo}_6L_6\text{O}_3\text{N}_3]^n\text{+/−}$ and $[\text{Mo}_6L_2\text{O}_3\text{N}_3]^n\text{+/−}$ molecular cluster units.
high flexibility of the inorganic matrix’s composition was also mentioned as an advantage for the synthesis of new nanocomposites, however, only few are still reported in the case of the 0D nanocomposites based on transition metal atom clusters. The main matrix used is SiO₂ and by far.

2.1. 0D nanocomposites

2.1.1. @SiO₂

It is necessary to mention that the first examples of SiO₂ nanocomposite based on transition metal atom clusters were related to bulk and not to 0D nanocomposites. For instance, at the end of the 80’s, Newsham has shown that [[Mo₆Cl₄]((OSiCH₃)₃)₂]²⁻ can be encapsulated in a silica matrix prepared by sol-gel route in methanol [71]. In 1994, Robinson et al. studied the nature of the interaction between commercial silica gel and [[Mo₆Cl₄]X₄]²⁻ (X = SO₃CF₃, Cl) cluster units in organic solvents and different pH conditions by a simple absorption process [72]. Both cluster units, [[Mo₆Cl₄]X₄]²⁻ and [[Mo₆Cl₄]SO₃CF₃]²⁻, were able to be strongly absorbed at the surface of the silica gel, which contains a high density of Si-OH groups. The authors concluded that clusters could be bound by either electrostatic or covalent interactions, which mainly depends, under the same conditions, on the apical ligand’s properties. Indeed, the cluster units with the less substitutional labile apical ligands, in this specific case X = Cl, was not covalently attached to silica gel. In opposite, the SO₃CF₃ ligands, which could be readily replaced by solvent molecules for instance, presented the opportunity to coordinate the cluster to Si-O- groups in basic condition or even adsorb the solvated cluster cation by ion exchange in acid condition. The problem of the apical ligands’ substitution is a very important issue for preparing the nanocomposites and for controlling their properties and it will be discussed several times in the following sections. Nevertheless, the main result of these studies of bulk nanocomposites was that the integrity of the [[Mo₆Cl₄]X₄]²⁻ cluster core could be maintained in this heterogeneous environment, even in the case of exchange of apical ligands by other ions or solvent molecules. These results were very important for the first synthesis of 0D silica nanocomposites (noted @SiO₂) based on [[Mo₆Br₄]X₄]²⁻ cluster units (X = Br, OH) in 2008 (Figure 3) [68]. Grasset et al. reported the synthesis of red-NIR luminescent [[Mo₆X₄]X₆]@SiO₂ nanoparticles (X = Cl, Br, or I) via a water-in-oil (W/O) microemulsion process wherein the nanosized [[Mo₆Br₄]X₆]²⁻ cluster units are homogeneously dispersed in high monodisperse silica nanoparticles (called homogeneous 0D nanocomposites) (Figure 4). Very shortly, the microemulsion is a thermodynamically stable dispersion of water droplets with a size about tens nanometers in oil phase, stabilized at the interface by amphiphilic surfactant molecules. Those water droplets, also called inverted micelles, constitute a suitable confined reaction medium for the synthesis of a wide variety of well-defined functional 0D silica nanoparticles with controlled size and architectures [30,32,221].

This process is quite simple and highly reproducible for preparing multifunctional @SiO₂ nanocomposites with complex architectures with a diameter around 50 nm (Figure 4). The key point in this microemulsion process for embedding nanosized metal clusters in 0D silica nanocomposites is to obtain stable colloidal solutions containing highly dispersed nanoclusters to avoid their aggregation and precipitation before the encapsulation [68].

![Figure 3](image1.png)

Figure 3. (a) Optical microscopy image of [[Mo₆X₄]X₆]@SiO₂ (X = Cl, Br, I) nanocomposites (powder between two plates of glass under irradiation at λexc = 546 nm). (b) Scanning electron microscope (SEM) images of [[Mo₆X₄]X₆]@SiO₂ 0D homogeneous nanocomposites. (c) Z-contrast high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) mode image of two adjacent [[Mo₆X₄]X₆]@SiO₂ nanoparticles. Adapted from 68 with permission from Wiley.

![Figure 4](image2.png)

Figure 4. Multifunctional nanoparticles with complex architectures. Adapted from 32 with permission from Springer.
The microemulsion was prepared by adding acidic Cs$_2$[Mo$_6$X$_8$]X$_e$$_e$ (X = Cl, Br, I) colloidal water/ethanol solution to a polyoxyethylene (4) lauryl ether/heptane mixture. Then, the precursor of silica nanoparticles, tetraethoxysilane (TEOS), was added to the microemulsion. The silica matrix was synthesized by increasing the pH inside the nanoreactors by adding an ammonia water solution, which catalyzes the TEOS condensation. The acidic solution, containing the Mo$_6$ nanoclusters, catalyzed first the hydrolysis of the monomeric species of TEOS, which consequently migrated into the nanoreactors for the condensation and formation of monodispersed @SiO$_2$ 0D nanocomposites after 2–3 days. Aubert et al. have confirmed that during the microemulsion process, the cluster units are losing a part of their Br apical ligands and counter cations [120]. The Br ligands are replaced partially by OH groups that can form hydrogen bonds with the silanol groups of the silica and by OSi groups through a covalent bonding between the cluster units and the silica matrix.

One of the goals of the preparation of these first [[Mo$_6$X$_8$]X$_e$$_e$]@SiO$_2$ functional silica 0D nanocomposites was to prepare relevant candidates in theranostic applications (bioimaging, labelling, photodynamic therapy (PDT), and so on). Indeed, functional silica nanoparticles present a strong potential for biotechnologies for decades [222–226]. silica constitutes a very good candidate as a matrix for the preparation of nanocomposites-based metal atom clusters thanks to its high chemical stability and biocompatibility. silica can prevent the degradation of the cluster units’ properties and, moreover, the surface of the SiO$_2$ matrix can easily be conjugated with various biomolecules and is water-soluble. Cytotoxicity is a very important issue for biotechnology applications. Aubert et al. showed that these [[Mo$_6$Br$_8$]X$_e$$_e$]@SiO$_2$ 0D nanocomposites (X = Br, OH, OSi) presented a dose effect but no time effect, and the cell toxicity became significant only for the fibroblastic cells and for the highest concentration (100 μg/mL) [120]. More interestingly, the in vitro cytotoxicity in spheroid models, examined by the acid phosphatase assay, revealed that this 0D nanocomposites induced a strong oxidative stress to model cancer KB cell lines ((ATCC® CCL-177) derived from a human epidermal mouth carcinoma [130]. In opposite, Cabello-Hurtado et al. showed that [[Mo$_6$Br$_8$]X$_e$$_e$]@SiO$_2$ have any phytotoxicity significant effect on plant cell growth and viability or photosynthetic efficiency on Arabidopsis thaliana [125].

Since this first example of 0D [[Mo$_6$X$_8$]X$_e$$_e$]@SiO$_2$ (X = Cl, Br, or I) nanocomposites, some studies have been published on the homogeneity of functional silica nanocomposites based on transition metal atom cluster compounds. For the Mo$_6$, this process was successfully used with the highly red-NIR luminescent (Bu$_4$N)$_2$[[Mo$_6$I$_8$](NO$_3$)$_6$] [124,135,191] and Cs$_2$[[Mo$_6$I$_8$](C$_2$F$_5$COO)$_6$] [123] cluster compounds. In 2010, it was expanded to Re$_6$ cluster compounds by Aubert et al. [88] and then very recently by Khazieva et al. [142]. Aubert et al. synthesized and characterized a new red-emitting @silica 0D nanocomposites based on A$_4$([ReX$_6$]X$_s$) metal atom clusters compounds (A = Cs or K, X = S or Se, and X$^2$ = OH or CN) with an interesting changing in the chemical process. Indeed, to prevent the precipitation of the clusters due to the low pH, the microemulsions were prepared by adding ammonia to the polyoxyethylene (4) lauryl ether/heptane mixture prior to the aqueous cluster colloidal solution and prior to TEOS, so both the hydrolysis and condensation steps in the silica synthesis were base-catalyzed. In 2018, the W/O microemulsion process was extended to positively charged Ta$_6$ nanoclusters [[Ta$_6$Br$_{12}$]H$_2$O$_6$]$_{12}$$^{+}$ by Chen et al. [199]. This new step could be very attractive for biotechnology applications because interestingly, over the past several decades, hexanuclear tantalum bromide clusters have attracted considerable attention, in particular as a commercial tool for the phase determination of large biological assemblies by X-ray crystallography and as radiographic contrast agents [227–230].

In parallel to this homogeneous 0D SiO$_2$ nanocomposites, it is also possible to use the microemulsion process to prepare more complexes bi- or multifunctional @SiO$_2$ 0D nanocomposites as presented in Figure 4. Compared to homogeneous 0D SiO$_2$ nanocomposites, complexes bi- or multifunctional @SiO$_2$ 0D nanocomposites combine in the same nanoparticles several properties such as magnetism, photoluminescent and/or plasmonic. For instance, magnetic nanocomposites could be handleable and sensitive to radiofrequency signals. The first example of bifunctional @SiO$_2$ 0D nanocomposites was done by Grasset et al. as early as 2008 by the controlled and nanostructured association of [[Mo$_6$Br$_8$]Br$_{12}$]$_{12}^{+}$ cluster units and γ-Fe$_2$O$_3$ nanocrystals [86]. These bifunctional 0D nanocomposites exhibit silica nanoparticles with regular spherical shape of 50 nm in diameter and the γ-Fe$_2$O$_3$ nanocrystals (6 nm) are located at the center of the nanoparticles whilst the [[Mo$_6$Br$_8$]Br$_{12}$]$_{12}^{+}$ cluster units are homogeneously dispersed around the magnetic core within the @SiO$_2$ matrix (Figure 5). The bifunctional character (magnetism and luminescence) of these nanocomposites has been evidenced by complementary techniques. The effect of the applied magnetic field, concomitant to the red emission, was directly observed in an aqueous ethanolic solution by using an optical microscope under irradiation at $\lambda_{exc}$ = 405 nm and an applied magnetic field (1.5 T). Very interestingly, the presence of γ-Fe$_2$O$_3$ as core does not affect the red luminescence properties of the cluster units, and an intense broad band with a maximum
Figure 5. Optical microscope images using $\lambda_{exc} = 405 \text{ nm}$ of dispersed nanoparticles under a magnetic field (1.5 T) showing the growth of a nanoparticles layer along the wall of a cell as a function of time. Adapted from 86 with permission from the Royal Society of Chemistry.

located at $\lambda_{cen} = 738 \text{ nm}$ was observed as expected for the $[[\text{Mo}_6\text{Br}^0_8]\text{Br}^0_6]^2^-$ cluster units. The zero field cooled-field cooled (ZFC-FC) magnetic behavior was typical of superparamagnetic ferrite nanocrystals dispersed in silica matrix [231,232].

In 2014, Nerambourg et al. improved this bifunctional nanocomposites by tuning the size of the magnetic nanocrystals (from 6 to 15 nm) and by preparing the first multifunctional nanocomposites (Figures 6 (a–f)) [155]. Indeed, gold nanoclusters (2 nm) were successfully generated on the surface of the $[[\text{Mo}_6X^1_8]X^6_6]^{-\gamma\text{Fe}_2\text{O}_3}@\text{SiO}_2$ by the direct nucleation of gold ions immobilized on their surfaces under UV light (Figure 6(g,h)). The goal was to obtain a hybrid nanocomposite that possesses luminescent, magnetic and plasmonic properties.

This strategy of multifunctional nanocomposites or decorated silica nanoparticles by nanoclusters was recently and nicely extended by Elistratova et al. and Fedorenko et al. [132,139]. Elistratova et al. introduced a facile and very interesting synthetic route to embed phosphorescent $[[\text{Mo}_6\text{I}^1_8]\text{I}^0_6]^2^-$ and $[[\text{Mo}_6\text{I}^1_8]$(CH$_3$COO)$^0_6]^2^-$ cluster units onto amino-decorated silica nanoparticles prepared by microemulsion.

High uptake capacity of the clusters (8700 of $[[\text{Mo}_6\text{I}^1_8]\text{I}^0_6]^2^-$ and 6500 of $[[\text{Mo}_6\text{I}^1_8]$(CH$_3$COO)$^0_6]^2^-$ per each nanoparticle) was possible thanks to the ionic self-assembly and coordination bonds between the charged nanoclusters and ionic (amino- and siloxy-) groups at the silica (Figure 7 upper). Fedorenko et al. mixed the previous works by the combination of superparamagnetic iron oxides at the center of the silica nanocomposites and $[[\text{Mo}_6\text{I}^1_8]$(CH$_3$COO)$^0_6]^2^-$ cluster units at the surface within amino-decorated group (Figure 7 lower).

Interestingly, very recently, Elistratova et al. extended this process to water insoluble cluster salts $(\text{Bu}_4\text{N})_2[[\text{Mo}_6\text{I}^1_8]$(L = CF$_3$COO- and C$_6$H$_5$F$_2$COO-) by using an additional layer of polyethylene imine (PEI) at the surface of the silica in order to significantly improve the colloid stability [143]. For the first time, this work highlighted the combination of pronounced PDT effect with high anticancer potential in the irradiation-free conditions using Mo$_6$-based silica nanocomposites. Khazieva et al. expanded this strategy to $[[\text{Re}_6\text{S}^0_8](\text{OH})^4_6]^4^-$ [142]. Most of these red-NIR luminescent nanocomposites could have applications in biotechnology field (in vitro bioimaging, cellular photosensitization, PDT, and so on) [233,234]. The strong potential of these nanocomposites as cellular

Figure 6. High-resolution transmission electron microscopy (HRTEM) images of (a) 6 nm, (b) 10.5 nm, (c) 15 nm (scale bar = 20 nm) $\gamma\text{Fe}_2\text{O}_3$ nanoparticles and the corresponding (d, e and f) $[[\text{Mo}_6X^1_8]X^6_6]^{-\gamma\text{Fe}_2\text{O}_3}@\text{SiO}_2$ 0D nanocomposites (scale bar = 100 nm). (g) TEM image of $[[\text{Mo}_6X^1_8]X^6_6]^{-\gamma\text{Fe}_2\text{O}_3}@\text{SiO}_2@\text{au}$. (h) zoom. Adapted from 155 with permission from Elsevier.
Figure 7. Upper: (a) Photos of silica nanoparticles in aqueous solution (1), silica nanoparticles in the cluster solutions (2) and assembled silica nanoparticles with clusters (3) before and after irradiation; (b) Schematic representation of self-assembly of the clusters complexes on silica surface; (c) TEM images of the silica nanoparticles and SiO₂@[(Mo₆L₆)L₆]. Adapted from 132 with permission of Elsevier. Lower: Schematically represented synthesis of Fe₃O₄@SiO₂@[Mo₆L₆] and TEM images of Fe₃O₄@SiO₂ (A) and Fe₃O₄@SiO₂@[Mo₆L₆] (B). Adapted from 139 with permission from Elsevier.
bioimaging agent has been revealed by cellular internalizations and flow cytometry measurements [123,124,132,139,142,143]. Neaime et al. reported the first preparation of transferrin grafted silica nanoparticles loaded by \([\text{Mo}_6\text{I}^\text{III}_6](\text{CF}_3\text{COO})^\text{4\text{a}}]\) metal atom clusters used for time-gated luminescence (TGL) bioimaging observation [123]. TGL imaging clearly showed that the conjugates accumulated around the nuclei upon internalization into living cells. Moreover, cellular imaging and pronounced PDT effects were observed, no matter, the localization of the cluster units (interfacial or encapsulation) [124,132].

To conclude on this part on 0D silica nanocomposites prepared by microemulsion process, we just mentioned that more ‘exotic’ 0D silica nanocomposites \(\beta\)-NaYF\(_4\)Yb:Er@NaYF\(_4\)@[\(\text{Mo}_6\text{Br}^{\text{III}}_8\text{Br}^{\text{VI}}\text{a}\)@SiO\(_2\) or ITO@[\(\text{Mo}_6\text{Br}^{\text{III}}_8\text{Br}^{\text{VI}}\text{a}\)@SiO\(_2\) (M = Nb, Ta) (ITO = indium tin oxide) were reported by Thangaraju et al. or Chen et al., respectively [98,175]. The latter case will be presented more in detail in the section related to films and coatings prepared by EPD for saving energy applications.

The microemulsion route is not the only way to prepare functional 0D silica nanocomposites and obviously the well-known ‘Stöber-Fink-Bohn’ process was one of them [235]. The first example of homogeneous 0D nanocomposite prepared by this simple process was reported by Dechelézelle et al. in 2010 and it was dedicated to the engineering of photonic colloidal crystals based on \([\text{Mo}_6\text{Br}^{\text{III}}_8\text{Br}^{\text{VI}}\text{a}\)@SiO\(_2\) (25 layers of silica microparticles with a diameter = 330 nm) by using the Langmuir–Blodgett technique [89]. These photonic structures exhibit strong angle-dependent luminescent properties. An inhibition of the emission intensity from the light sources was observed in the spectral region of the stopband, which follows the Bragg-Snell law as the angle between the [111] direction and the incident beam was varied. Moreover, the incorporation of one or several planar defects (monolayer of silica microparticles with a diameter = 450 nm) within the periodic structures gives rise to the creation of a passband in the stopband. In the energy range of this passband, an increase of the emission intensity has been found. In the same year, Gao et al. reported the encapsulation of several positively charged phosphine-terminated (III) chalcogendie clusters (\([\text{Re}_8\text{Se}^{\text{IV}}_8]\{(\text{Et}_3\text{P})^\text{2}\text{I}_2\}^\text{1}\), \([\text{Re}_8\text{Se}^{\text{IV}}_8]\{(\text{Et}_3\text{P})^\text{2}\text{Br}^{\text{IV}}\text{Br}\}^\text{2}\), \([\text{Re}_8\text{Se}^{\text{IV}}_8]\{(\text{Bu}_3\text{P})^\text{2}\text{I}_2\}^\text{1}\), and \([\text{Re}_8\text{Se}^{\text{IV}}_8]\{(\text{Bu}_3\text{P})^\text{2}\text{Br}^{\text{IV}}\text{Br}\}^\text{2}\) in silica nanoparticles (10–20 nm) for singlet oxygen production and PDT applications. Surprisingly, the encapsulation was ineffective for neutral and anionic clusters [90]. Two years later, Kirakci et al. prepared singlet oxygen photocative composite materials by incorporating (Bu\(_3\)N\(_2\))[\(\text{Mo}_6\text{I}^\text{III}_6\](CF\(_3\)COO)\(_{4\text{a}}\)] cluster compounds into silica particles with sizes about 10 nm or 500 nm [47]. Interestingly, the intensive luminescence of the smallest \([\text{Mo}_6\text{I}^\text{III}_6]\{(\text{CF}_3\text{COO})^\text{4\text{a}}\}^\text{2\text{a}}\]@SiO\(_2\) nanoparticles was completely and effectively quenched by oxygen. In contrast, the bigger microparticles were not affected by oxygen, which suggested that a high fraction of nanoclusters is not accessible to oxygen because of the large size of the silica microparticles. The comparison of the photo-physical properties of this nanocluster with those of the archetypal complexes \([\text{Ru}(bpy)_3]^{2\text{a}}\) and \([\text{Ir}(ppy)_3]\) illustrated the relevance of this nanocomposites. The last case is related to the work performed by Vorotnikov et al. on the detailed investigation of silica microparticles (500 nm) incorporating of various quantities of \((\text{Bu}_3\text{N})_2\)\([\text{Mo}_6\text{X}^{\text{III}}_8\](\text{NO}_3)^\text{4\text{a}}\] (X = Cl, Br, I) cluster compounds [133,191]. These studies revealed that hydrolysis of the molybdenum cluster precursors during the ‘Stöber-Fink-Bohn’ process strongly affects both morphology and photo-physical parameters of the materials, especially at high loadings. Low loadings of the nanoclusters demonstrated the most promising set of properties (i.e. the highest photoluminescence quantum yields and efficient singlet oxygen generation) for cellular internalization of proteins, such as the HIV TAT protein (HIV: human immunodeficiency viruses; TAT: Trans-Activator of Transcription) and commercial protein delivery agents (e.g. Pierce®).

The two last examples of original chemical route to prepare 0D SiO\(_2\) nanocomposite based on metal atom clusters are related to the work of Nguyen et al. [116] and de la Torre et al. [236]. In the first work, commercial pseudocube hollow silica nanoparticles (HSNs) (SiliNax SPPN(b)), supplied from Nittetsu Mining Co., Ltd) were used and the \([\text{Mo}_6\text{I}^\text{III}_6\]X\(_{4\text{a}}\)\] (X = Cl, CF\(_3\)COO) nanoclusters have been successfully embedded into the HSNs and/or deposited at their surface by a vacuum impregnation process (VIP) at room temperature (Figure 8). The HSNs were clearly filled by the Mo\(_6\) nanoclusters as confirmed by HRTEM coupled energy-dispersive X-ray analysis (EDX), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Brunauer–Emmett–Teller (BET) analysis. The results of the UV-Vis and photoluminescence spectra demonstrated that the optical properties of the Mo\(_6\) cluster-functionalized HSNs nanocomposites were still retained even when annealed at 200°C.

In the second example, de la Torre et al. used amino-decorated mesoporous silica nanoparticles MCM-41 as containers. They incorporated the hexanuclear molybdenum cluster \((\text{Bu}_3\text{N})_2\)\([\text{Mo}_6\text{I}^\text{III}_6\](\text{CH}_3\text{CO}_2)\_6\] by a simple electrostatic assembly. Basically, an aqueous solution of cluster units (0.035 M) containing Pluronic® F-127 (0.3 mM) was mixed with an aqueous suspension of APTES@MCM-41 (0.5 g L\(^{-1}\) (APTES: 3-Aminopropyltriethoxysilane). The mixture was shaken for 10 min and then sonicated for 15 min. Finally functionalized @MCM-41 nanoparticles were
separated by centrifugation at 9000 rpm, washed with water and dried under vacuum. The highly specific surface area of these nanoparticles (1000 m²/g) guarantees a very good dispersion of the nanocluster, as corroborated by electron microscopy analysis. The activity of this new photosensitizer for PDT was tested in cancer cells and this nanocomposite exhibits a good activity against human cervical cancer (HeLa) cells whereas free cluster compound showed practically no photoactivity, probably due to poor cellular uptake and degradation inside the cell [236].

Finally, these studies suggested a potential application as insulating material prepared by efficient and very simple methods.

2.1.2. Nanocrystals clusters assemblies: @ZnO, @TiO₂, @Au

Surprisingly, since 2008, only few 0D nanocomposites based on other oxides than SiO₂ were reported for optical (for instance, (Bu₄N)₂[Mo₆Br₄]Br₄@ZnO) or catalytic (K₃[(Re₉S₈)(CN)$_{11}$]-Cu(OH)$_3$@TiO₂) applications, this leaves the door open to many experiments in the future [84,87,111]. In the first paper by Grasset et al., the main idea was to induce synergetic optical effects between the semiconductor nanocrystal and the nanoclusters. Indeed, the photoemission studies showed that [[Mo$_6$Br$_4$(X$_6$)$_2$] clusters units (X = Br or OH) can efficiently interact with ZnO nanocrystals, not only in the colloidal solution, but also in solid-state conditions confirming an immobilization of the units on the ZnO surface. As reported above, NaYF₄: ITO and iron oxides nanocrystals were mixed with nanoclusters, but there are no clear synergetic effects between both components.

Very recently new nanocomposites emerged with gold nanoparticles as core and several studies demonstrated the synergetic effect of the association with Mo₆ nanoclusters as shells for plasmonic applications or photodynamic and photothermal therapies [168–170]. Novikova et al. demonstrated that a partial overlap of the photoemission spectrum of the [[Mo$_6$I$_8$]I$_6$]$_2$ (L = NO$_3$– and $p$-toluenesulfonate) clusters and the surface plasmon resonance band of the spherical gold nanoparticles facilitated energy transfer between the both photoactive components. Specifically, by a careful control of the spacing between the cluster shell and the gold nanoparticle with an SiO₂ layer (21 nm), a significant increase in luminescence and photosensitizing properties of the nanocomposites was achieved. In parallel, the cluster complex facilitated energy conversion to heat by gold particles and hence increased the heating rate under laser irradiation [168]. These properties can be even improved by optimizing the aspect ratio of the gold

Figure 8. Upper: (a) Sketch of the vacuum impregnation process (VIP) and the possible movement of the air and the nanoclusters (b) STEM image of [[Mo$_6$Br$_4$]((C$_6$F$_5$)COO)$_6$]@HSNs and the overlapped EDX mapping image of the Mo element on the HSNs. (c) the UV-Vis reflectance spectra of: HSNs (black), HSNs mixed with [[Mo$_6$Br$_4$]((C$_6$F$_5$)COO)$_6$] without the VIP (red dot), [[Mo$_6$Br$_4$](Cl)$_6$]@HSNs (blue) and [[Mo$_6$Br$_4$]((C$_6$F$_5$)COO)$_6$]@HSNs with the VIP (red line). Adapted from 116 with permission from Elsevier.
nanorods [169]. Sciortino et al. show, very recently, that the plasmon resonance energy of gold nanoparticles (100 nm) can be tuned over a large area of the visible spectrum, from 2.4 to 1.6 eV, by changing the thickness of the [(Mo8Br8)(NCS)6] nanocluster shells between 0nm and 70 nm. Interestingly, the plasmonic response was performed at nanometer resolution on individual nanoparticles using electron energy-loss spectroscopy (EELS) directly inside a TEM [170].

2.2. 2D nanocomposites

The second illustration of the powder nanocomposites is related to layered materials (2D) as matrices or supports (graphene-, layered hydroxides- and boron nitride(BN)-based materials). All these materials are mainly interesting for their (photo)catalytic properties.

2.2.1. Graphene

In 2013, Barras et al. reported the first example of gold nanoparticles/Na2[Mo8Br8(N3)6] nanoclusters deposited on graphene oxide nanosheets (GONs) and its photocatalytic activity [109]. This nanocomposite exhibits a high photocatalytic activity for the degradation of organic molecules (ex: rhodamine B) under visible light irradiation. Nevertheless, the synthesis of this cluster compound with N3 ligands is explosive and complicated to safely managed. In 2015, Kumar et al. replaced this unstable nanocluster by the very well known and safe Cs2[Mo8Br8Br6] and (Bu4N)2[Mo8Br8Br6] nanocluster compounds [112]. The proof of the loading of these Mo8 nanoclusters on GONs was probed by Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), HRTEM and EDX analysis. These new nanocomposites presented an activity for visible light induced photocatalytic reduction of carbon dioxide into methanol. One year later, very interestingly, Feliz et al. extended the catalytic activity of these nanocomposites to photocatalytic hydrogen evolution reaction (HER) from liquid water under homogeneous and heterogeneous conditions by using (Bu4N)2[Mo8Br8Br6][F6] nanocluster as starting precursors [94]. In this specific case, the catalytic activity of the [Mo8Br8]4+ is enhanced by the in situ exchange of the apical F ligands by OH ligands and the generation of [(Mo8Br8)F6,5(OH)1.5]2− cluster units at the surface of the GONs. Nevertheless, it was observed that the covalent grafting of the nanoclusters on the surface of GONs limited the accessibility to the nanocluster active sites for the catalytic reaction and altered the lattice sp2 structure of graphene, which results in defects and a loss of electronic properties. Feliz et al. proposed recently to solve this issue to use the [(Mo6Br8)(C2F5COO)6]2− cluster units and to add pyrene groups as counter cations of this cluster units as noncovalent interactions on the graphene surface [115]. The pyrene moieties act simultaneously as energy transmitters and as supramolecular linkers between the cluster anions and graphene. The production of green H2 from sunlight is one of the most important targets for low-carbon energy production in the future in order to reduce the global warming and this beautiful work including a supramolecular strategy opened up wide perspectives in terms of research prospects to design better nanoclusters/GONs nanocomposites for H2 production.

2.2.2. Layered hydroxides

During the last decade, there was a growing interest of the synthesis of heterostructured nanocomposites using layered hydroxides (monolayer = LDHs, double layer = LDHs) because of their unique two-dimensional (2D) lamellar structural features and properties for heterogeneous (photo)catalysis, water treatment, agriculture and biotechnology applications for instance [237–242].

Regarding the layered hydroxide nanocomposites functionalized with octahedral metal atom clusters, there are only few examples, two were reported by Christiano et al. in the eighties [69,70] and the two others very recently by Nguyen et al. [117,217]. The first two examples were focused on the intercalation in Na+-Montmorillonite of [Mo4X12]n+ (M = Nb, Ta; n = 2–4) and [Mo6Cl8]4+ cluster cores by ion exchange process. The nanoclusters have been converted to metal oxide pillared forms with potential utility for oxidation catalysis [69,70]. The third example was dedicated to the synthesis of a new zinc-aluminum layered double hydroxide (Zn2Al-LDH)-based nanocomposite functionalized with the [(Mo6Br8)6Cl3]2− cluster units. LDHs are composed by octahedral hydroxide layers occupied by divalent and trivalent metals with the general formula of [M2+1-xM3+x(OH)2]x+x[A−n]x/n)mH2O (x as the molar ratio M2+(M2+(M3+) in the range 0.2–0.33) (M2+ = Cu, Zn, Co, Mg, Cr...; M3+ = Al, Fe, Th…). The metal hydroxide layers are positively charged and are neutralized by negatively organic or inorganic ions (A=NO3, CO32, SO42, F, Cl or alkyl anions) accompanied by the absorption of the interlayer water molecules. Generally, these negatively charged molecules control
the interspace between two metal hydroxide layers and can be exchanged by bigger molecules in order to expand it [243]. This strategy was used by Nguyen et al. by replacing NO$_3$ by n-dodecyl sulfate anions (CH$_3$(CH$_2$)$_{10}$CH$_2$OSO$_4$) [117]. Indeed, the interlayer distance value, estimated by X-ray diffraction (XRD), for the starting LDH-1 is about 0.9 nm, which is too narrow to intercalate the cluster units with a size of 1.2 nm. This space is extended to 2.7 nm in the LDH-2 by the intercalation of n-dodecyl sulfate anions. Then, the [(Mo$_6$Cl$_6$)$_2$]Cl$_4$ anionic clusters were simply introduced into the LDH-2 by an anion exchangeable method in dimethylformamide under ambient conditions (Figure 9). The addition of the nanoclusters induced an exfoliation, an interlayer expansion (up to 5 nm) and an amorphization of the LDH-2. Again, a part of the apical ligands of the nanoclusters are exchanged during the synthesis process and all the results support for the possible chemical bonding between the [(Mo$_6$Cl$_6$)$_2$Cl$_4$(OH)$_3$]$_2^-$ or [(Mo$_6$Cl$_6$)$_2$Cl$_6$(H$_2$O)$_3$]Cl$_4$($OH$)$_2$ anionic clusters or [(Mo$_6$Cl$_6$)$_2$Cl$_6$(H$_2$O)$_3$] neutral cluster and the hydroxide of Zn-Al LDH-2. The efficiency of the degradation of the methylene blue was evaluated at more than 90 wt% after 2 h by using the Mo$_6$@LDH-2 nanocomposite with the existence of H$_2$O as an optimal co-agent.

Very recently, a simplest one-pot synthesis was proposed by Nguyen et al. to prepare copper LHSs nanocomposites (noted Mo$_6$@CHN) mixed with A$_2$ [(Mo$_6$X$_3$)$_2$X'$_n$] nanocluster compounds (A = Cs, Bu$_4$ N; X = Cl, Br and I), the last example [217]. In this process, monoclinic copper hydroxynitrate (CHN), was fabricated in the presence of the nanoclusters by simply mixing an ethanolic solution of Cu(NO$_3$)$_2$·3 H$_2$O and a solution of nanoclusters dispersed in acetone (Figure 10(a)), followed by thermal treatment at 80°C for 3 h. The precipitate powder was collected by centrifugation and washing several times, then dried at 100°C. XRD and HRTEM analysis confirmed the presence of CHN, whereas photoluminescence and XPS study proved the existence of the integrity of the [Mo$_6$X$_3$]$_{14}^{4+}$ cluster cores even after the thermal and chemical treatments. Unlike Mo$_6$@Zn$_2$AL-LDH nanocomposites, the clusters do not fit between the layers but only at the surface in the case of Mo$_6$@CHN. The expected chemical formula of the Mo$_6$@CHN nanocomposites was estimated to be [(Mo$_6$X$_3$)$_2$X'$_n$($OH$)$_z$]Cl$_4$·yH$_2$O. A high catalytic degradation rate of methylene blue after 30 minutes was reached by using the Mo$_6$@CHN/H$_2$O$_2$ systems. The reuse of the system was demonstrated up to 4 reaction cycles with an excellent efficiency (Figure 10(b)).

2.2.3. h-BN

The last example of 2D materials is related to the preparation of nanocomposite based on hexamolybdenum nanoclusters and exfoliated hexagonal boron nitride (h-BN) nanosheets [118]. h-BN is known to have high thermal conductivity, stability toward high temperatures and aggressive chemical conditions (acids, bases, and oxidants) and some catalytic properties. The cluster deposition on the exfoliated h-BN nanosheet surface was obtained by their impregnation by a (Bu$_4$N)$_2$[(Mo$_6$X$_3$)$_2$] (X = I, NO$_3$) in acetone solution. Interestingly, again, the possibility to play with the apical ligands of the cluster units was used to control the interaction with the matrix. The cluster units with the more labile apical ligands, NO$_3$-, gave the best results, because of the replacement of NO$_3$ by OH and water molecules able to undergo in situ hydrolysis resulting in formation of an insoluble thin amorphous film of [(Mo$_6$I$_6$)(H$_2$O)$_2$](OH)$_2$·yH$_2$O on a modified h-BN nanosheet surface.

To resume this section on 0D and 2D nanocomposites based on transition metal clusters, it was clearly demonstrated that if their potential is noticeably important, there is still a lot of room for new original systems. Indeed, nanocomposites based on silica matrix represent the vast majority of the examples reported to date for the 0D and the use of 2D materials as support for the metal atom clusters is apparently important for developing new (photo)catalysts. Indeed, these studies

![Figure 9](image_url)

**Figure 9.** (a) Powder-XRD patterns of LDH-1, Mo$_6$@LDH-1, LDH-2, Mo$_6$@LDH-2 with the indications of the planes of 003 (●), 006 (●), 009 (●) and the lozenge symbol (●) assigned for the ZnO phase. (b) Schematic of the process to fabricate the LDH and designed structure of its nanocomposite. Adapted from 117 with permission from Elsevier.
evidence that nanocomposites based on transition metal atom clusters are very promising new materials in many important catalytic fields like the elimination of pollutants or the production of green H\textsubscript{2} and other areas related to environmental protection. The choice of the matrix is very important, for example, inert and biocompatible silica is a good compromise for biotechnology applications, whereas more active matrix support (for instance, copper hydroxynitrate, metal or semiconductor) are necessary for catalytic or photonic applications. One conclusion of these works is that the incorporation of metal atom clusters into matrix supports enhances their stability, their photoactivity and could improve their cellular uptake, compared to free clusters. Moreover, a novel 1D hybrid lead perovskite \textit{[[\text{Re}_{6}\text{S}_{6}](\text{PzH})_{6}][\text{Pb}_{3}\text{I}_{6}(	ext{DMF})_{2}]]-6\text{(DMF)}\text{ with hexarhenium cluster cations has been synthesized recently by Ly et al. \textsuperscript{[167]}}} This original study introduces a new class of nanocomposites and opens a promising path to materials with great potential for optoelectronic applications in photonic devices with broadband emission and stability. The maturity of this scientific field is still far from being reached.

3. Thin films and coatings

Thin films and coatings, with thickness ranging from nanometers to a few tens of micrometers are playing a very important and indispensable role in daily life with a global material market valued around USD
8000 million in 2020 and it is expected to reach USD 8500 million by the end of 2027 for end-user industries [243]. Nevertheless, as is known, main transition metal atom clusters compounds based on Nb₆, Mo₆, Ta₆, W₆, Re₆ are ceramic-like materials [37–67], which clearly and strongly limit their application for thin films and coatings. In this review, conventional coating methods (dip coating, drop-casting, spin-coating, and so on), which were applied for nanocomposite metal cluster-based films highly dispersed in a matrix, will be developed at the end of this section. We will first focus on the use of the EPD for the fabrication of pure octahedral cluster-based and nanocomposite thin films, which is a real breakthrough in this field. This well-known industrial technic was developed first for transition metal atom clusters in the International Research Laboratory ‘Laboratory for Innovative Key Materials and Structures’ (IRL 3629 LINK) at the National Institute for Materials Science in Japan [193]. Similarly to the previous section several kinds of octahedral metal clusters were used with different positions of inner ligands; face-capped [[M₆L₆]La]m/n− and edge-bridged [[M₆L_{12}]L₆a]m/n cluster units. Both of them own the charge on the cluster units, a key point for the success of EPD.

3.1. EPD

EPD is an advanced technique for thin films and coatings due to its versatile and cost-effective process, simplicity, and the scaled-up possibility to large product volumes and sizes. In general, EPD acts as electrochemical equipment; an electric field is applied between two electrodes that force the charged particles to move toward the oppositely conductive electrodes, called electrophoresis. Then, the accumulation of the charged particles by physical interaction will form a condensed layer on the surface of the electrodes, called deposition. EPD has been applied for metal oxide, traditional ceramic materials, and advanced materials with μm-sized or submicrometric (d > 100 nm), for example, functional ceramic coatings, porous materials, laminated ceramics, functionally graded materials, thin films, and nanostructured materials [244–247].

To date, the EPD technique was developed for a variety of nano-architecture materials, including nanorods, nanowires, nanotubes, and nanosheets [248]. The approach of EPD on antibacterial coatings also attracted huge interest for biomedical applications with promising results [249]. Thanks to the driving force induced by the electrical field, highly concentrated colloidal solutions are not required (compared to conventional deposition process) and generally the deposition time is low, from tens of second to several tens of minutes. Nevertheless, the most interesting point of EPD is to fabricate pure metal cluster-based thin film with no matrix or binders that is limited or almost impossible to achieve from other methods.

3.1.1. EPD of [(MoBr₃Br⁺)²⁺ cluster units: the model case

In 2016, for the first time, Nguyen et al. revealed that an amorphous Mo₆ cluster-based thin film deposited on ITO-coated glass (ITO glass) could be successfully fabricated by using the EPD process at a low applied voltage (13 V) and very short deposition time (30 s) [193]. In this work, the dispersing medium of face-capped [(Mo₆Br₄]Br⁺)²⁻ cluster units, deposition time, and the applied voltage of EPD were preferably optimized to retain the chemical composition, octahedral structure as well as photostability.

Methyl ethyl ketone (MEK) was selected as the most suitable dispersing medium for the Cs₃[(Mo₆Br₄]Br⁺) cluster compound to obtain the homogeneous and transparent film (Figure 11(a)). Importantly, the luminescence of the Mo₆ clusters excited at 370 nm was retained in some cases (Figure 11(b)). Indeed, the solvent affects the dissociation of [(Mo₆Br₄]Br⁺)²⁻ anion and counter cation, and the hydrolysis reaction at the surface of the electrode during EPD. The hydroxyl group created during the EPD process by hydrolysis reaction increased the exchange of the apical ligands, resulting in modification of the optical properties. The unique and nanometer-size structure composed of metallic core and surrounding ligands contributed to the distinct EPD mechanism in comparison with other materials. In 2017, an EPD mechanism for this Mo₆ metal cluster-based film was proposed by Nguyen et al. [198] Complementary experimental techniques (XRD, XRF, HRTEM, Electrospay ionization-mass spectrometry, SEM-EDX, XPS, IR, and so on) clearly demonstrated that the microstructure of the films is heterogenous and dense (Figure 12). The most important part of the film is composed by an amorphous stacking of nanoclusters with the general formula, [H₃O⁺]₂[(Mo₆Br₄]Br⁺)₄(OH)₄]. The closest part (few ten nanometers) to the ITO glass substrate is enriched in Br anions and in aggregated nanoclusters based on the zero-charged clusters, [Mo₆Br₄]Br⁺)₄(H₂O)₄]. The size of these Mo₆ zero-charged clusters was confirmed by TEM that showed many spherical nanoparticles of about 6 nm (Figure 12(a)). The role of the counter cations, inorganic (Cs⁺) and organic (N(n-C₃H₇)₄)+ compositions, was investigated to understand their effect on the dissolution of the cluster in MEK. Cs⁺ cation was confirmed to be eliminated from the Mo₆ film by presenting Cs 3d region in the XPS spectrum (Figure 12(b)) while the disappearance of (n(n-C₃H₇)₄)⁺ (TBA⁺) cation was confirmed by FTIR spectrum. These counter-cations are mainly exchanged by H₂O⁺ in the film. Regarding the cluster units’ structure, the binding energy of Mo 3d was retained after EPD which meant the octahedral structure was stabilized (Figure 12(c)).
Interestingly, the binding energy peak of Br apical ligands was reduced in Br 3d regions that explained the loss of two bromide apical ligands (Figure 12(d)). Moreover, the FTIR spectrum suggested the increase of the OH group in the EPD film. The Br/Mo atomic ratio in the film was sharply decreased during the first 10 s of the deposition and low voltages, then finally reached the value close to the theoretical index (2.33) at 40 s and 17 V (Figure 12(f)). Based on all these results, a scheme of the film suggested the heterogenous layer structure and hydrogen bonding interaction between the components was proposed (Figure 12(g)).

In summary, a mechanism of the Mo6 film performance by using EPD was proposed: (i) the exchange of 2 Br apical ligands by OH− or H2O groups in solution, (ii) Cs+ and TBA+ cations are mainly replaced in the film by H3O+ to neutralize the negative charges of the Mo6 nanoclusters at the electrode surface, and (iii) two kinds of clusters, that is, [Mo6Br4Br6(Oh2)] and [H3O]2[Mo6Br4Br6(OH)2], mainly composed the dense film (Figure 12(e)). Even though a slight modification of luminescent emission peak was recognized due to the change of the Mo6 cluster network, the obtained EPD film showed high transmittance in the visible range and strong absorption in UV and NIR ranges. Stabilization of the thin film in air and moisture was an issue and free-cracking Mo6 cluster thin film was prepared by the use of a top-coating Polydimethylsiloxane agent of the Mo6 film [95]. These optimized parameters of EPD on the Mo6 cluster motivated many achievements after that.

3.1.2. Sensor

Very recently, the light-dependent ionic-electronic conduction on pure Mo6 thin film prepared by EPD was demonstrated and studied by Harada et al. [153] The micron-size Mo6 cluster film presented an ionic conductivity (Figure 13). Interestingly, this conductivity can be controlled and tuned by temperature and humidity. Activation energies at the relative humidities (RH) of 50 RH% and 80 RH% were estimated at 68 kJ/mol and 50 kJ/mol, respectively (Figures 13(a, b)). In addition, the H3O+ counter cations coordinate with the substituted OH− groups at the Br6 sites by hydrogen bonding, and many water molecules would be similarly linked by hydrogen bonds around it (Figure 13(c)). As the result, the existence of HO−−H+−OH− bridges between adjacent cluster units and activation energies seem to favor the vehicle diffusion model [250]. Moreover, the electronic conduction of the MC film greatly changes depending on the wavelength (from UV to red) and intensity of the irradiated light. The effect of photons on the electronic properties of ionic conductors at room or low temperature is a new and interesting research field [250, 251]. These unique multi-sensing properties would present new possibilities for environmental sensor applications.

3.1.3. Absorber for solar cell: from DSSC to all-solid

The discovery of the possible deposition by EPD of pure molecular Mo6 atom clusters opened the way to all-solid solar cells for photovoltaic applications. In the frame of the LINK project, Renaud et al. first reported the use of the iodide Mo6 clusters as an inorganic absorber for dyed sensitive solar cells (DSSC). By using EPD, high-quality, mesoporous TiO2 (n-type) photoanodes and NiO (p-type) photocathodes containing homogeneous, amorphous layers of the Mo6 cluster were successfully prepared [99]. The use of EPD greatly improved the homogeneity and the concentration of the Mo6 absorber coated in porous photoelectrodes, compared to the classical soaking method (Figure 14) [93]. The UV-Vis absorption characteristic of the Mo6 cluster (Mo6I4I2)2−, one of the clusters exhibiting one of the strongest absorptions in visible light range, was retained after being deposited on both kinds of photoelectrodes (Figures 14(a,b)).
The multilayer structure of the Mo₆ cluster-coated photoelectrode was confirmed in the SEM image with the deposition of the Mo₆ cluster on the surface and inside the pore (Figures 14(c,d)). For the photoelectrodes prepared by EPD, the photoconversion efficiency is clearly improved by 35–300%, according to the type of electrolyte or semiconductor comparison with a soaking method (Figures 14(c,f)). Beyond the performance of the DSSC cells composed of the transition metal cluster, these promising results will open the new pathway for the investigation of photoelectronic applications, ranging from photoelectrochemical devices (PEC) to all solid solar cells. The future challenge in using the Mo₆ cluster as a non-toxic alternative in optoelectronic devices (stable under atmospheric conditions) is to optimize the band alignment between the cluster and the n-type transparent semiconducting oxides in order to favor an effective charge transfer.

In parallel, to these results on DSCC solar cells, Renaud et al. claimed, for the first time, the potential of the Mo₆ cluster-based nanoarchitectonic owning the characteristic as ambipolar materials [104]. Ambipolar material is known as new semiconducting compounds in which holes and electrons can intrinsically transport and transfer simultaneously [252,253]. In this unique case, the thin films of the aqua-complex-based compound [[Mo₆I₈]I₄(H₂O)₂]xH₂O prepared by EPD...
was studied through an in-depth photoelectrochemical performance. The charge transport properties depended on the potential values in dark or under light and the behavior of the electrodes (n-type and p-type) (Figure 15(a)). All electrodes (Fluorine doped tin oxide (FTO), MC film, MC pellet) were demonstrated a straight line with a positive slope characteristic of n-type conductivity, favoring electron transport in the MC compound (Figure 15(b)). The MC iodide absorber composed of the photoelectrode of the all-solid solar cell was measured the current-voltage characteristics in the dark and under AM1.5 illumination (1000 W m⁻²) of this p-i-n junction (Figures 15(c,d)). The photosresponse demonstrated the hole and electron injection from the MC layer to semiconducting electrodes with the similar lifetime and opposite directions, a proof of ambipolar behavior. These charge carrier transports are possible to cross the solar cell because of the full adequacy between the energy levels of each layer (Figure 15(e)). The nanoarchitectonic materials based on transition clusters open a potential in the field of photovoltaics for the collection of light and the generation of electron/hole pairs.

**3.1.4. Pathogenic bacterial biofilms**

The last example of thin film prepared by EPD of pure Mo₆₆ nanoclusters is reporting the recent work of Kirakci et al. on very promising coating for mitigation of pathogenic bacterial biofilms under blue light [138]. They utilized EPD to prepare dense layers of the Na₂[Mo₆₆I₆(OPO₃H₂)₆] (1) and [Mo₆₆I₆(OOC₆H₄PPh₃)₆]-Br₄ (2) clusters compounds deposited on ITO coated glass (Figure 16(a)). The MC layers showed high transparency and thickness of about 1 micron even though the morphology existed big particles (Figure 16(b)). The photoexcited MCs created singlet oxygen O₂(¹Δg), which was able to inactivate several pathogens. The study revealed that continuous irradiation of 460 nm light on the EPD film resulted in strong antibacterial properties on Gram-positive *Staphylococcus aureus* and *Enterococcus faecalis*, as well as, Gram-negative *Pseudomonas aeruginosa* and *Escherichia coli* bacterial strains (Figures 16(d,e)). Both layers displayed strong inhibition of the biofilm growth, and moreover, the film with the cluster 1 is also able to eradicate of matured biofilms, which is very interesting. These Mo₆₆ cluster-based photoactive layers are attractive for the design of antibacterial biofilm activated by visible light and reduce the harm of UV/blue light due to production of red light or oxygen sensing. The study of the electrophoretically photoactive MC film on the fight against infective microorganisms under blue light opens a new strategy for the mitigation of pathogenic bacterial biofilms.
Figure 14. Comparison of the optical properties between (a) CMI@TiO$_2$@FTO and (b) films CMI@NiO@FTO prepared by EPD at 20 V and 15 V for 30 s, respectively, or soaking method (for 48h) from a CMI solution at 17 mM in acetone. (c) SEM image of a cross-section a CMI@NiO@FTO photoelectrode obtained at 10 V for 30 s and (d) EDS analyses on the mesoporous NiO/CMI layer. Comparison of photoresponses in the dark (dash lines) and under AM$_{1.5}$ illumination (1000 W.m$^{-2}$, solid line) of photovoltaic cells prepared from (e) CMI@TiO$_2$@FTO and (f) CMI@NiO@FTO photoelectrodes colored by soaking method or by EPD during 30 s at 20 and 15 V, respectively. The used electrolytes were the I$^-$/I$_3^-$ and the cobalt complex CMI@TiO$_2$@FTO and CMI@NiO@FTO photoelectrodes, respectively. Reproduced from 99 with permission from Elsevier.

Figure 15. (a) Nyquist plots of the electrochemical circuit in the dark and under illumination at OCP and the equivalent circuit used to fit them. (b) Mott–Schottky plots for the MC film deposited on FTO, the FTO substrate, and the Cs$_2$[Mo$_6$I$_8$]$^{i-}$ dense pellet depicted vs RHE by using the formula $V_{fb}$(RHE) = $V_{fb}$(Ag/AgCl) + 0.059 pH + $V_{Ag/AgCl}$(RHE). (c) MC-based all-solid solar Cell, (d) I(V) measurements in the dark and under AM1.5 Illumination, (e) energy levels of each layer on an absolute scale with respect to vacuum. Adapted with permission from 104. Copyright 2022 American Chemical Society.
3.1.5. UV and NIR blocking transparent thin films for window application

Previous results demonstrated that EPD is the most relevant technique to prepare pure Mo₆ metal cluster-based thin film, however, for unknown reasons yet, it failed to be applied for some Mo₆ clusters containing for instance the distinctive characteristic of the apical ligand (Cl or OCOC₂F₅). In similar way, even if Ta₆ or Nb₆ nanoclusters could be deposited as a single component, their instability in air is too high to prepare stable pure functional films (see for instance [96]). To overpass this problem, small amount of polymer was used as binders to support the dispersing ability of the clusters and their chemical stabilization. For instance, transparent films containing [(Mo₆Cl₄)²⁺(OCOC₂F₅)]₂⁻ cluster unit and [(Nb₆ X₄)X₆⁺]₄⁺ (X = Cl, Br) cluster units were fabricated by using EPD with the support of poly(methyl methacrylate) (PMMA) as a stabilizing binder. Transparent thin films were obtained with thicknesses of about 1.5-micrometer. They exhibited strong absorption in range of UV and NIR light as well as high transparency in range of visible light (>60%), and an improved stability against moderate temperature and humidity conditions [207]. As these specific Mo₆ and Nb₆-based cluster units, a Ta₆-based cluster dispersed in MEK was successfully deposited on the ITO-coated glass by EPD as the first example [96]. However, the film quality was opaque with the existence of big particles. There were specific phenomena that needed to be clear in this original work. First, the green-colored [[Ta₆(Br)₁₂(H₂O)₆]²⁺ species was stable in water, however, it is failure to prepare film by EPD. Second, by using ketones (acetone or MEK) as a good dispersing medium for EPD, a brown Ta₆-based cluster film was successfully deposited on an anodic electrode as seen in Figure 17(a). This unwanted changing of color was simply explained by the oxidation of the clusters from [[Ta₆(Br)₁₂](H₂O)₆]²⁺ to brown-colored [[Ta₆(Br)₁₂(H₂O)₆]³⁺ cluster units. Considering the kinetics of the oxidation and the necessity to use ketone as solvents for EPD, an investigation of the addition of water was carried out by Nguyen et al. Films containing green-colored [[Ta₆(Br)₁₂(H₂O)₆]²⁺ unit species were successfully fabricated with adding a small amount of water (Figure 17(b)). However, again it was impossible to maintain the green color for several days at room temperature in air due to the high reactivity of the Ta₆ cluster units. Finally, it was found that polyvinylpyrrolidone (PVP) was an excellent stabilizer of the green-colored [[Ta₆(Br)₁₂(H₂O)₆]²⁺ cluster species to obtain the homogeneous films and to improve their transparency using an optimized EPD process (Figures 17(c,d)). Films with a transparency upper than 60% in the visible and strong absorption in the UV and NIR light ranges were obtained (Figure 17(e)). The efficiency in energy saving of these new UV-NIR filters was estimated by the determination of different figure of merit (FOM) values, such as T_S, T_V, and T_S/T_V (T_S = solar transmittance and T_V = visible transmittance), and the color
coordinates ($x$, $y$, and $z$). The $T_{vis}/T_{sol}$ ratio of the Ta-based thin film is equal to 1.25 for the best films that is potential result for energy saving window-based applications.

As mentioned in the 0D SiO$_2$ nanocomposites section, Ta$_6$ and Nb$_6$ cluster units were embedded into SiO$_2$ nanoparticles by reverse microemulsion method [98,199]. These 0D nanocomposite were used to prepare the first all inorganic film nanocomposites. HAADF-STEM images of ITO@Ta$_6$@SiO$_2$ NPs indicated a core-shell structure of about 76 nm averagely with the presence of discrete ITO nanoparticles occupied in the center. In addition, the Ta$_6$ cluster units were uniformly dispersed with a size of 1 nm in the whole SiO$_2$ shell. (Figure 18(a)). The elements (Si, O, In, Ta, and Br) were confirmed in the EDS spectrum that proved the successful synthesis of ITO@Ta$_6$@SiO$_2$ NPs (Figure 18(b)). Thanks to the negative zeta potential of ITO@Ta$_6$@SiO$_2$ NPs in acetone, EPD was successfully applied to fabricate the ITO@Ta$_6$@SiO$_2$ film with the relative thickness (0.9–1.5 microns) (Figure 18(c)). As expected, these ITO@Ta$_6$@SiO$_2$ films showed strong absorption in the UV light range with high transparency and the appearance of a band of 800 nm, which indicates the improvement toward energy saving applications (Figure 19(d)) [98].

### 3.1.6. Photodetector

Silica is not the only inorganic matrix available for preparing all inorganic nanocomposite thin films based on transition metal atom clusters.

Very recently, Nguyen et al. demonstrated the possibility to use LDH matrix [151]. By using EPD, a thin and transparent Cs$_2$[Mo$_6$I$_8$P$_6$]-functionalized LDH film (3 μm) was successfully prepared with a dense lamellar structure (Figure 19(a)). It was revealed that these films exhibited several interesting complementary properties, that is, (i) a red emission centered at the wavelength of 690 nm by UV-Vis light irradiation, (ii) an anionic conductivity of about $10^{-6}$ S.cm$^{-1}$ with...
an activation energy ($E_a$) of about 1.08 eV, (iii) a proper photocurrent response under UV-Vis light excitation ranging from 320 to 540 nm, and (iv) a photocurrent response depending on the film thickness, temperature, and humidity (Figures 19(b,c)). The remarkable point in this study is the determination of the relation between the photocurrent and the temperature or the humidity, which has not been figured out, to the best of our knowledge, in previous reports about LDH-based materials [254–257]. The reproducibility and stabilization of the sample’s photocurrent response were established. The excellent photoconductivity properties sensitizing with temperature and humidity obtained from the electrophoretic Mo$_{6}$-functionalized LDH films supported application potential for photo-humidity sensing and a photodetector.

This section clearly shows that this field of research is really new and has very strong potential in key areas for the future (PV, mitigation of pathogenic, sensors). The use of EPD to fabricate thin films based on clusters of transition metals is a real breakthrough. Considering the importance of the activity on thin films in the economy and the already active use of EPD in industry, we can imagine that this strong potential will be materialized by innovations very soon.

### 3.2. CSD processes

As explained in the previous section, EPD can be used for the fabrication of pure octahedral cluster-based and nanocomposite thin films with no matrix or binders thanks to the charge on cluster units. In parallel, more conventional coating methods such as spin-coating, dip-coating or drop-casting are also efficiently employed despite the ceramic-like aspect of metallic clusters synthesized by solid-state chemistry. Indeed, as already mentioned molecular MC can be solubilized in many solvents which facilitates their coating process. Furthermore, the advantage of such process lies in the fact that it is possible to modify the chemistry, that is, the ligand nature or the VEC before the deposition. The main issue is to control these parameters during all the shaping process.

Depending on the application or the property that needs to be enhanced, MC can simply be associated with a binder [80,92,105–107,144] to facilitate the chemical solution deposition (CSD) process or it can be part of a more elaborate devices including several layers [107,156,160], ink [187], polymer dispersed liquid crystal [101], quantum dots and nanocrystals [102,171,192] or DSSC electrodes [93,97].

#### 3.2.1. Photonic and photovoltaic devices

Thanks to their high phosphorescent properties, Mo$_6$ and Re$_6$ nanoclusters are actively used for optical thin film and coating devices. Indeed, the development of luminescent thin films and coatings free of heavy metal or rare earth elements is an important issue for environmental reasons and energy efficiency. The first examples of such hybrid nanocomposites were reported in 2013 [156,171]. Aubert et al., first reported a ZnO-C$_{52}$[Mo$_6$Br$_3$Br$_6$]@PVP film with an average thickness of 3 µm [171]. The properties of such films were improved later by Truong et al. by replacing the bromine nanoclusters by a more efficient, C$_{52}$[Mo$_6$I$_3$(OOC$_2$F$_2$)$_2$] [192]. Interestingly, in these similar processes, nanocomposite colloids of ZnO nanocrystals and Mo$_6$ nanocluster compounds were prepared by very simple and low-cost solution chemistry including PVP as matrix. The resulting solutions have been used to fabricate highly transparent and tunable luminescent films free of heavy metals or rare earth elements. The luminescence properties of the later system are highly tunable (from yellow to red emission) and the emission wavelength is strongly dependent on the ratios between ZnO and CMIF amounts and the excitation wavelength. In parallel, in 2013, Zhao et al. prepared novel transparent...
luminescent solar concentrators devices composed of phosphorescent Mo₆ chloride nanoclusters [92]. The near-perfect absorption cut off at the edge of the visible spectrum (430 nm) and the massive Stokes shift to the near-infrared (800 nm) of these nanoclusters allows for efficient and selective harvesting of ultraviolet (UV) photons, improved reabsorption efficiency and non-tinted transparency in the visible spectrum. Since, these pioneer works, excellent results were obtained by several groups in the world for light emitting devices [156,160] or transparent luminescent solar concentrators [101,102].

3.2.2. UV and NIR blocking transparent thin films for window application

Previous section mentions that Nb₆ or Ta₆ nanoclusters could be deposited by EPD technique but it needs more steps than with Mo₆. Their instability in air has to be considered by using a binder. Recent studies focus on the chemistry of niobium and tantalum clusters from an experimental and a theoretical aspect [61,106]. It helps to understand some mechanisms and properties of the cluster units \([M_6X_{12}L_n]^{n/-}\) \((M = Nb, Ta; X = Cl, Br; L = X, H_2O; 2 \leq n \leq 4)\) in the solid-state and in solution. Ta₆ clusters show a strong...
absorption in UV, whereas Nb₆ clusters present a great absorption in NIR (Figure 20(b)). Starting from this advancement, heterometallic clusters, that is, \([\text{Nb}_6-x\text{Ta}_xX_{12}]\text{L}_x^{3-x/2} (1 \leq x \leq 5)\) have been synthesized and studied. Their UV and NIR blocking capacity were evaluated according to their VEC [105,106].

\([\text{Nb}_6-x\text{Ta}_xX_{12}]\text{H}_2\text{O}^{2+} (X = \text{Cl, Br})\) cluster units are stable in water and can be then integrated in organic (PVP) or hybrid (SiO₂-PEG) matrix by drop-casting or Mayer rod coating process in a reproducible way (Figure 21(a)). These matrices agree with a solar application (transparency, cost, implementation), can be shaped with a thickness of a few tens of micrometers (Figure 21) and are prepared in aqueous solution without extra steps. Furthermore, it is possible to control the VEC and so, the optical properties of the cluster units from their solubilization to their integration into the matrices. Experimental and theoretical studies highlight which oxidation state of the integrated cluster units should be selected for a solar control application. Nb₆ and heterometallic Nb₆Ta clusters show higher NIR shielding at VEC 16 whereas Ta₆ clusters need to be oxidized to VEC 15 to absorb in the NIR region. However, VEC 14 has to be avoided for homo and heterometallic clusters because of their low UV and NIR absorption. Based on their electrochemical potential in water, SnX₂ (X = Cl, Br) (Figure 21(b)) and Fe(NO₃)₃ have been used during the process to keep Nb₆ and Nb₆Ta clusters at VEC 16 or to oxidized Ta₆ clusters to VEC 15, respectively. Optical properties were maintained throughout the process and evaluated for the obtained nanocomposites.

As well as for films obtained by EPD, FOM values \((T_{\text{vis}}, T_{\text{sol}}, T_{\text{vis}}/T_{\text{sol}}, S_{\text{NIR}})\) and color coordinates were measured for films obtained by CSD process. \([\text{Nb}_6X_{12}]\) (VEC = 16) and \([\text{Ta}_6X_{12}]\) (VEC = 15) cluster cores show similar values of \(T_{\text{vis}}/T_{\text{sol}}\) (1.27–1.29) when integrated in PVP films on a glass substrate. The highest values were reached with \([\text{Nb}_6\text{Ta}_4X_{12}]\) (1.30–1.33) and even higher by including an ITO layer (1.73) (Figure 21(c)). Indeed, the NIR shielding of clusters mainly absorb between 700 and 1100 nm, whereas NIR reflection of ITO is above 1200 nm. Their association allow to get rid of almost all the NIR solar radiation and to obtain excellent \(T_{\text{vis}}/T_{\text{sol}}\) and \(S_{\text{NIR}}\) values. By comparison, a perfect solar control material can be simulated with a film that transmits 90% of visible light, and absorbs 100% of UV (200–400 nm) and NIR (780–2500 nm). Its \(T_{\text{vis}}/T_{\text{sol}}\) ratio would be 1.85.

4. Conclusions

It has been clearly demonstrated that the remarkable properties of the octahedral transition metal atom clusters can be largely preserved and enhanced in the form of nanocomposites. Introduction to various Nb₆, Mo₆, Ta₆, W₆, Re₆ molecular nanoclusters in nanocomposites with two-dimensional, one-dimensional and zero-dimensional morphologies has been presented in this review paper. Matrices ranging from organic polymers to inorganic layered oxides can be used and adapted to the targeted applications. The clear potential and synergetic effects of these nanocomposites for biotechnology applications, PV, solar control, catalytic, photonic and sensor applications was strongly demonstrated. Indeed, the incorporation of metal atom clusters into matrix supports enhances their stability, their photoactivity and could improve their cellular uptake for biotechnologies, compared to free clusters. This review also provides a basic level of understanding how nanocomposites are characterized and processed using different techniques and methods. As a new strategy, the electrophoretic deposition process appears to be very efficient to fabricate highly transparent, homogeneous and functional nanocomposite thin films and coatings.

Of course, this field of research is quite young and new challenges and opportunities using transition metal clusters as building blocks for multifunctional nanocomposites are numerous. This field can be extended to the use of other transition metal clusters, such as titanium, vanadium, copper, zirconium or even heterometallic systems as already started by Lebasterd et al. [105,107,257–262]. This family of nanoclusters is extremely rich and could be even probably enriched by using machine learning methods [263–265]. Controlled self-assembly of nanoclusters could play a key role in customizing advanced functional materials via collective and synergetic properties between neighbored building blocks [266]. As briefly mentioned in the introduction, the condensation and dimensionality of the metal atom clusters influence strongly the electronic properties and an association with an adequate matrix could generate new nanocomposites. For instance, the mixing of MCs with semiconductor nanocrystals could also be very interesting for photovoltaic applications. Moreover, to increase the dimensionality of the metal atom clusters could be very interesting in terms of thermal stability for instance, which is still a weak point for the molecular nanoclusters.

Furthermore, recently, calculations suggested that Nb₆ or Ta₆ clusters could be used for new material design, for instance as cations in hybrid organic-inorganic perovskites, as a substitute for toxic Pb. Indeed, band gaps, band alignment, and hydrogen adsorption calculations show that the designed cluster-based hybrid perovskites have potential as intermediate-band materials for photovoltaics, and as photocatalysts for the hydrogen evolution reaction [267]. Another possibility is to use these transition metal atom clusters as precursors for the discovery of new compounds and nanocomposites like nitrides, carbides, borides, sulfides or alloys [218,268–271]. The field of possibilities is open to everyone and the adventure of the nanocomposites based on metal atom clusters has only just begun.
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