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REVIEW

Molybdate-based Nanocrystalline Materials for Efficient Environmental Remediation and Electrochemical Energy Conversion Applications: An Update

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Molybdate-based nanocrystalline materials have been considered as promising candidates in various energy and environmental remediation applications owing to their distinct characteristics and versatile functionalities. This article furnishes a comprehensive overview of recent advancements that have been made in synthesis techniques, characterization and applications of molybdate-based nanocrystalline materials in the realm of energy transformation and ecological restoration technologies. Molybdate-based nanomaterials may be classified as sulfides, phosphates and mixed-metal compounds which can be synthesized effectively by wet chemical method. The mechanisms underlying the enhanced performance of molybdate-based nanocrystalline materials are interpreted, along with strategies for improving their efficiency and stability.

Keywords: Metal molybdates, Organic pollutants, Photodegradation, Electrochemical supercapacitor, Energy storage.

INTRODUCTION

The recent surge in industrialization has given rise to two pressing global concerns, *viz.* the energy crisis and environmental pollution. Many sectors heavily depend on non-renewable energy sources, such as fossil fuels, are finite and depletable coal, oil and natural gas, resulting in significant carbon dioxide emissions during combustion. This reliance on fossil fuels contributes to the sustainability of the overall carbon footprint, exacerbating environmental concerns and contributing to climate change [1-5]. Efforts are being taken in developing more sustainable and renewable energy materials for mitigating these emissions and fostering a cleaner and more environmentally friendly future [6-10]. Generally, pollutants liberated from traditional energy sources are reported to harm the environment and contributes to pollution and global warming.

Technology and industry advancements are mainly impacting the environment with diversified pollutants. Production of inexpensive mass-produced items have raised environmental concerns, particularly regarding generating waste products that harm local ecosystems. For example, textile manufacturing companies may adversely affect the water quality and aquatic life by discharging untreated wastewater into nearby streams. This practice threatens essential resources such as water, as contamination is crucial for the survival of all living things present in water [11-14]. Nanoparticles, characterized by their diminutive size and expansive surface area, significantly contribute to the enhancement of their catalytic properties. However, despite their small size, semiconducting metal oxides exhibit a wider band gap than metal nanoparticles. Modification of their synthetic processes, incorporation of dopant elements and creation of composites are essential to tune their physico-chemical properties [15].

Textile effluents pose a significant environmental threat as they contain aromatic amines that may exhibit a detrimental impact on the survival of fauna and flora. Without proper pretreatment measures, the groundwater system may be severely contaminated with substituted phenols, dyes and agricultural wastes [16,17]. Dyes are categorized according to their colour, uses and composition. Rhodamine B dye and 4-nitrophenol have been considered to be dangerous contaminants found in water systems. The act of releasing dyes into surface waters not only deteriorates water quality but also triggers biochemical toxicity, particularly due to the presence of azo bonds (-N=N-) within the dye compounds [18,19]. Reactive dyes, commonly associated with respiratory problems, contain most carcinogenic dyes and their breakdown products. Consequently, it is imperative to address the release of such pollutants to mitigate the adverse impacts on water quality and human health [20]. The specific diseases associated with the exposure of these substances can vary depending on the type of pollutants or dyes, exposure duration and concentration of the pollutants.

The increasing global water scarcity and inadequate availability of pure water underscore the need for the innovation of versatile materials designed for the remediation of wastewater [21]. Over the past decades, there has been a diverse array of techniques devised and employed in the field of water treatment. These encompass essential approaches such as screening, filtration, centrifugation, *etc*. Various other methods include, separation procedures based on ultrafiltration, crystallization, sedimentation, gravity separation, flotation, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion-exchange, electrodialysis, electrolysis and adsorption. Due to the availability of broad range of adsorbents and ease of operation, adsorption is a particularly good option for treating water. This versatile approach can effectively target soluble and insoluble organic, inorganic and biological pollutants. Its applicability extends to source reduction and reclamation, catering to the diverse needs of potable, industrial and various other water purposes [22].

Environmental remediation by photodegradation: In a similar vein, photodegradation emerges as an attractive water treatment approach, involving the chemical breakdown of large molecules into smaller, non-toxic counterparts utilizing solar radiation across a broad spectrum. Photodegradation works by use of light-induced photocatalytic processes, which simplify redox reactions and enable the effective oxidation or reduction of organic contaminants. This process begins with the absorption of photons in the UV, visible and infrared spectral ranges. By directly converting light energy into chemical energy, photodegradation positions itself as a promising and energy-efficient technology that provides a way to break down and get rid of toxic organic substances. Complete pollutant mineralization, ease of use, lack of toxic byproducts, economy and ability to operate at room temperature and standard atmospheric pressure are some of its advantages over traditional methods [23-28]. Metal molybdates are emerging in photocatalysis and metal molybdates have a lower band gap compared to the other nanocrystalline materials.

Electrochemical supercapacitors: On the other hand, fossil fuels currently serve as the predominant energy source to sustain proliferation. Nevertheless, escalating rates of consumption have spurred the request for energy sources that are effective in their usage and next-generation storage solutions. In past few years, there has been a notable amount of change exploitation of renewable energy sources like wind, tide and solar to meet the growing energy need. Within this context, batteries and supercapacitors have emerged as crucial technologies, with supercapacitors garnering increasing attention. This is attributed to their high power densities, impressive cycle lifespans (exceeding 1,000,000 cycles), excellent rate capabilities, rapid charge/discharge rates and cost-effectiveness [29-34].

In the current era, there is a growing imperative evolution from conventional fossil fuels to renewable energy sources like solar and wind power. This shift is driven by concerns over the finite reverses of fossil fuels and the significant environmental pollution they cause. However, the sporadic character of renewable energy sources poses a challenge to achieving a consistent electricity supply on a large scale, hindering its widespread adoption in the grid. To overcome this challenge, developing effective electrical energy storage systems is crucial. These systems play an important role in storing the variable output of renewable sources and ensuring a stable power supply for practical applications. Electrochemical energy-conversion systems (EES) enable the conversion between chemical and electrical energy, providing a means to store and release energy as needed. While EES devices have found widespread use in portable electronics, electric vehicles and even grid applications, they still face limitations, particularly in terms of energy density and cycling stability. Addressing these challenges is essential for further enhancing the viability of electrochemical energy storage and facilitating its integration into the energy infrastructure [34-38].

Despite various names such as "supercapacitor" by Nippon Electric Company and "ultracapacitor" by Pinnacle Research Institute, the primary functionality remains consistent: energy storage between a solid electrode and an electrolyte. Notably, General Electric pioneered supercapacitor technologies in 1957, being the first to demonstrate and patent them. Since then, supercapacitors have remained a focal point for academia and industry [39-48]. A supercapacitor is a type of energy storage device comparable to secondary batteries, known for its high specific capacitance, elevated power density and extended cycle life. Supercapacitors are often employed in conjunction with batteries to fulfil start-up power requirements, particularly due to their superior power density. There are different types of supercapacitors categorized by their energy storage mechanism, such as electrical double-layer capacitors (EDLC) and pseudocapacitors or ultracapacitors. In EDLC, charge accumulation occurs near the electrode/electrolyte interface. EDLCs exhibit higher power density than redox capacitors due to substantial charge accumulation, while redox capacitors provide greater energy density owing to a larger potential window than EDLCs [48-52].

The mechanical and chemical stability of electrode materials during repeated charge and discharge cycles greatly influence the cycle stability. Ensuring robust structural integrity and resistance to chemical degradation is crucial for maintaining a high-performance supercapacitor electrode over an extended operational lifespan [53-56]. The electrode material primarily influences the charge storage capacity of electrochemical energy storage devices. Studies indicate that conventional power electrodes, featuring active material coatings, suffer from drawbacks such as high production costs, low active material utilization rates and limited service life. Consequently, the pivotal task in advancing electrochemical energy storage devices with enhanced performance and cost-effectiveness lies in identifying and adopting appropriate novel electrode materials [57].

Molybdenum based materials: Molybdenum resources on earth are abundant, with China boasting the largest share globally, comprising 44% of known reserves. The United States closely follows with a 28% share, while Chile holds the third position, possessing 13% of the total molybdenum resources. Consequently, these three nations collectively dominate most global molybdenum reserves. In recent times, researchers have directed significant attention toward metal molybdate compounds $MMoO_4$, where M = Sr, Ba, Ca, Mg and Ni, among others. These compounds have demonstrated exceptional properties across various applications, sparking considerable interest in the scientific community. Nanocomposite incorporating diverse metal molybdate components has been successfully synthesized, capitalizing on the synergistic effects derived from the combination of these elements. Presently, diverse and practical fabrication techniques are employed to tailor specific methods, sonochemical methods, combustion methods, sol-gel methods and solid-state methods [58]. Selective metal molybdates are discussed in the following sections in detailed manner.

Nickel molybdates: Kianpour *et al*. [59] synthesized $NiMoO_4$ nanostructures using a straightforward co-precipitation method involving nickel benzoate as nickel source and ammonium heptamolybdate as molybdenum source. The experimental section outlined deemed suitable for large-scale synthesis of nickel molybdate nanostructures. Additionally, the calculated band gap of the $NiMoO_4$ nanostructures suggested its potential application as a photocatalyst. Photocatalytic properties were assessed through the photooxidation of methyl orange (MO), revealing a 60.7% degradation of MO after 90 min of UV light irradiation. These findings underscore the promising photocatalytic capabilities of the synthesized nickel molybdate nanostructures. Alborzi *et al.* [60] prepared $NiMoO_4$ nanoparticles through a surfactant-free sonochemical method in an aqueous medium. The high purity of the synthesized $NiMoO_4$ nanoparticles was confirmed by EDS and XRD analyses and the VSM analysis revealed a paramagnetic behaviour. Ramulu *et al.* [61] reported a cost-effective hydrothermal method to produce binder-free, porous $NiMoO_4$ nanoparticles. When employed as a photocatalyst, nanocrystalline $NiMoO_4$ demonstrated a significant 67% degradation of methyl orange after 60 min of UV light irradiation. These findings highlighted the potential of obtained nanocrystalline $NiMoO_4$ as a promising material for nanoflower/nanosheet-decorated Ni foam for a super battery electrode. The resulting nanohybrid structure featured increased active sites and interconnected networks, enhancing the electrolyte diffusion and electrokinetics. The electrode comprising calcined nickel molybdate nanofibers/nanosheets supported on nickel foam demonstrated excellent electrochemical performance with a specific capacity of 216 mA h/g, retaining ~100% capacity after 5000 cycles. The assembled device demonstrated notable energy storage performance, achieving a maximum energy density as 13.2 Wh/Kg with a power density of 400.1 W kg^{-1}. These findings suggest the potential of metal molybdates with nanohybrid composites for high performance energy storage.

Metal-doped nickel molybdates: The efficacy of Mn doping in improving the electrochemical performance of $NiMoO_4$ nanostructures has been demonstrated. Through the hydrothermal synthesis, Mn-doped $NiMoO_4$ nanostructures were grown and optimized for Mn content, resulting in a significant specific capacitance of 1262.6 F g^{-1} at 1 A g^{-1}. Remarkably, even after 14,000 cycles at 50 A g^{-1}, they retained 74.4% of initial capacitance [62]. In a supercapacitor setup, employing Mn-doped $NiMoO_4$ nanostructures as the positive electrode and activated carbon on carbon cloth/carbon nanotubes as negative electrode, an outstanding energy density of 64.95 W kg^{-1} was achieved at a power density of 864.5 W kg^{-1}. Additionally, the asymmetric supercapacitor displays substantial cycling stability, maintaining after 5000 cycles at 20 A g^{-1}, the device retains 77% of its initial capacity. This enhanced performance is attributed to stable reactions resulting from the synergistic interplay between nickel and manganese elements, along with rapid conduction facilitated by $NiMoO_4$ [62]. β-$NiMoO_4$ nanosheets, efficient visible light photocatalysts, were synthesized for degrading methylene blue under diffused sunlight and ultrasound. Achieving 98% degradation in 150 min, comparable to top materials, the nickel content in the nanosheet structure catalyst enhances photocarrier generation, moreover, the ultrasonic treatment enhanced the catalyst dispersion, ensuring the combined effect of light and sound generates oxidative radicals for efficient dye generation [63].

rGO and polymer-based nickel molybdates: A two-step procedure was used to produce a ternary nanocomposite made up of $NiMoO_4$, reduced graphene oxide (rGO) and polypyrrole (PPy) as an active material in a supercapacitor with flexibility electrodes. First, a hydrothermal technique was used to generate the $NiMoO_4$/rGO binary nanohybrid on flexible nickel foam. This produced hydrated nickel molybdate nanostructures with mixed morphologies at various temperature treatments and a honeycomb-like nanorod. The second step involved the *in situ* polymerization of PPy conducting polymer on coated nickel foam. The interaction of morphology, specific surface area and electrical conductivity in charge storage is shown by structural, morphological, porosity and electrochemical investigations. In 2 M KOH electrolyte, the highest specific capacitance of $NiMoO_4$/rGo-450/PPy nanocomposite was 1805 F g^{-1}. A flexible all-solid-state asymmetric supercapacitor device ($NiMoO_4$/rGO-450/PPy//AC/graphite) with a PVA/KOH gel electrolyte and separator demonstrated a maximum specific capacitance of 218.3 F g^{-1}. The material demonstrates an impressive energy density of 436.65 Wh kg^{-1}, coupled with a power density of 600 W kg^{-1}. Furthermore, it exhibits sustained electrochemical performance even when subjected to flexibility tests in a bent state [64].

Strontium molybdates: A straightforward method using sound waves in water successfully created tiny $SrMoO_4$ structures. These structures were confirmed to be highly pure based on EDS and XRD analysis. Further examination of their shape and size, influenced by additives like glucose and lactose, was conducted using SEM and UV-visible spectroscopy. The resulting nanostructures were spherical, approximately 50-55 nm in diameter, with an energy gap of 3.25 eV. When used as a photocatalyst, the $SrMoO_4$ nanoparticles led to a significant 73% degradation of methyl orange after 60 min of UV light exposure [65]. The nanostructures of $SrMoO_4$, synthesized using a wet chemical approach, proved to be efficient electroactive materials for supercapacitors. The electrodes demonstrate a specific capacitance of 384 C g^{-1} at a scan rate of 5 mV s^{-1}, indicating a significant cycling stability with 91.1% retention over 5000 cycles at a current density of 1 A g^{-1}. The combination of Sr and Mo enhances electronic conductivity, leading to a substantial energy density of 67.3 Wh kg^{-1} and a power density of 3150 W kg^{-1}. The distinctive characteristics of the nanostructure, including ample redox sites and short ion diffusion paths, contribute significantly to improved electrochemical performance and stability. Moreover, this environmental friendly synthesis method proves effective for developing advanced supercapacitor electrode materials [66]. A cation vacancy solid solution in $Sr_{1-3x}Bi_{2x}\Phi_xMO_4$ ($0 \le x \le 0.225$) was synthesized *via* the pelletizing method. Phases with $0.025 \le x \le 0.15$ exhibited a favoured tetragonal scheelite structure. The photocatalytic activity resembled $SrMoO_4$ for x values of 0.025 to 0.10 in rhodamine B dye photolysis. At $x = 0.15$ and 0.20, rhodamine B dye degradation under acidic pH showed a remarkable 92.7% removal with a 30 min treatment and 200 mg of catalyst. These findings suggest the potential use of this material in rhodamine B dye removal, particularly for x values of 0.15 and 0.20, using solid-state synthesis and degradation conditions [67]. $SrMoO_4$ has also been shown to have photocatalytic and electrocatalytic characteristics for the degradation and determination of diphenylamine (DPAH) [68]. In 45 min, it was found in UV-visible experiments that 99% of the DPAH had been photodegraded. Through controlled trials, it was found that for efficient degradation, the ideal catalyst loading, concentration and pH were 50 mg/mL, 20 mg/L and 12, respectively. Scavenger profile analysis indicated that the predominant active species $OH^{\bullet}$ radicals were the main factor influencing the degradation rate.

GCN doped strontium molybdates: A grinding-roasting technique was used to develop a new $SrMoO_4$/*g*-C_3N_4 (SMCN) nanocomposite. Through the photosensitization method, the synthesized composite demonstrated an effective photocatalytic activity in tetracycline and dyes. When the photocatalytic reaction was carried out in the presence of light, it showed more photoactivity than pure *g*-C_3N_4. Within 90 min, the percentages of tetracycline that were degraded by catalysts containing 25%, 10%, 15% and 20% SMCN, 62%, 66% and 73%, respectively. A pseudo-first-order model of tetracycline degrading process was fitted to provide a more accurate comparison of the photocatalysts' performance of mentioned above. It was found that the tetracycline degradation rates for SMCN containing 10%, 15%, 20% and 25% $SrMoO_4$ were 0.0139, 0.0140, 0.0171 and 0.0103 min^{-1}, respectively. Compared to pure *g*-C_3N_4, these rates were significantly greater (0.0029 min^{-1}). Among the prepared SMCNs, 20% SMCN showed the fastest rate of degradation, which was roughly six times faster than *g*-C_3N_4. This provides a highly efficient and stable photocatalyst for room temperature tetracycline or dye degradation [69].

Barium molybdate: A sonochemical method for synthesizing $BaMoO_4$ nanostructures using leucine and proline amino acids as capping agents was reported Gholami & Maddahfar [70]. It was reported that varying the amino acid type influenced the nanostructure size and morphology. These nanostructures exhibit room temperature ferromagnetism and efficiently degrade methyl orange (75%) under UV light. Bazarganipour [71] prepared a rod-shaped and spherical-shaped barium molybdates nanostructures *via* a sonochemical method using $Ba(Sal)_2Na_2MoO_4{\cdot}2H_2O$ at low temperature and pressure conditions. The manipulation of surfactant and power sources allowed to control the morphology of barium molybdate nanostructures. These synthesized nanostructures exhibit promising potential for various analytical applications, particularly in the efficient removal of methylene blue dye, with a remarkable uptake exceeding 85% with a short duration of 40 min.

Metal-doped barium molybdates: Rani *et al.* [72] synthesized pure and samarium-doped barium molybdate ($BaMoO_4$) nanostructures for application in supercapacitors. The X-ray diffraction (XRD) and Raman spectroscopy confirmed successful samarium incorporation within the $BaMoO_4$ host lattice. The study achieved controlled particle size by optimizing the dopant concentration. The 20% Sm-doped $BaMoO_4$ electrode exhibited an impressive capacitance of 281 F g^{-1} at a low scan rate of 10 mV s^{-1} in the cyclic voltammetry (CV) profile and 135 F g^{-1} at a high current density of 1 A g^{-1} in the galvanostatic charge-discharge (GCD) profile. Furthermore, this optimized electrode demonstrated remarkable long-term cycling stability, retaining 83.38% of its capacitance after 5000 cycles.

Calcium molybdates: $CaMoO_4$ nanoparticles were synthesized using a straight-forward hydrothermal method and subsequently evaluated for their electrochemical characteristics in both three-electrode and two-electrode configurations [73]. In the three-electrode setup, these nanoparticles exhibited specific capacities of 118.25 and 50 mAh g^{-1} at discharge rates of 2 and 20 A g^{-1}, respectively, while maintaining cyclic stability for over 6000 cycles. These nanoparticles were then utilized in the construction of aqueous asymmetric supercapacitors (ASCs), with $CaMoO_4$ serving as the positive electrode and AC as negative electrode. At a current density of 0.5 A g^{-1}, the material demonstrated a high Q_s value of 25.77 and at 5 A g^{-1}, it showed a specific capacity of 18.32 mAh g^{-1}. Furthermore, the minimal differences in electrochemical impedance spectroscopy parameters were observed even after 5000 cycles in the galvanostatic charge-discharge analysis, indicating efficient ionic mobility within the ASC device. When two ASCs were connected in series, they successfully powered 12 LEDs and a motor fan, underscoring the promising potential of $CaMoO_4$ nanoparticles for advancements in energy storage technology. Similarly, Hosseinpour-Mashkani *et al.* [74] successfully synthesized rod-like $CaMoO_4$ nanostructures *via* a surfactant-free sonochemical route. The photocatalytic activity of the nanocrystalline calcium molybdate was assessed, showing a 70% degradation of methyl orange under UV light irradiation for 60 min. The UV-visible absorption analysis revealed a pristine tetragonal phase of $CaMoO_4$ nanostructure with a band gap of 3.1 eV, achieved without supplementary heat treatment.

Carbon-doped calcium molybdates: Undoped $CaMoO_4$ and $CaMoO_4$ doped with 1%, 2% and 3% carbon were synthesized and assessed for their effectiveness by Chawda *et al*. [75]. The results revealed the photocatalytic degradation of methylene blue increased upon carbon doping, with the highest rate of degradation achieved using 2% carbon-doped $CaMoO_4$. Beyond this concentration, further carbon doping had a slightly adverse effect on the degradation rate. A proposed mechanism for photocatalytic degradation involved the participation of hydroxyl radicals as active oxidizing species, which was corroborated by scavenger studies using 2-propanol, resulting in a significant reduction in the degradation rate. Malachite green can also undergo photocatalytic degradation in the presence of both undoped and carbon-doped $CaMoO_4$ as reported by the same authors [76]. The carbon doping increases the photocatalytic activity of $CaMoO_4$ and the highest rate of degradation achieved while using 2% carbon-doped $CaMoO_4$. The optimal degradation conditions for malachite green include a pH of 9.7, a dye concentration of 5.00×10^{-5} M, 0.12 g of photocatalyst and a light intensity of 50.0 mW cm^{-2}.

Manganese molybdates: The rod-shaped $MnMoO_4$ crystalline structures featuring 2D nanoflakes were successfully synthesized *via* a wet chemical method aided by polyvinyl pyrrolidone (PVP) as reported by Cao *et al*. [77]. This study highlighted the PVP's significant influence on regulating the size distribution of these rod-shaped crystals. When utilized as electrode material for supercapacitors, these $MnMoO_4$ rods demonstrate a remarkable specific capacity of 109 C g^{-1} at 1 A g^{-1} current density over 2000 cycles. At higher current densities of 2 and 4 A g^{-1}, capacities of 93.9 C g^{-1} and 75.8 C g^{-1} were achieved, representing 86% and 69% of the capacity recorded at 1 Ag^{-1}, respectively. The 2D structural feature facilitates improved interfacial interaction between the electrolyte and $MnMoO_4$, facilitating electrolyte diffusion and charge transfer processes. Li *et al*. [78] synthesized a core-shell CoS-0.4/MMO/rGO/NF nanostructure *via* a simple hydrothermal reaction followed by electrodeposition. The impact of CoS shell mass loading on morphology and electrochemical performance was thoroughly investigated. The intercrossed network structure and synergistic effects of manganese molybdate (MMO) and CoS contribute to the exceptional specific capacitance of 3074.5 F g^{-1} at 1 A g^{-1}. Moreover, the assembled ASC delivers a high energy density of 50.3 W h kg^{-1} at 415.8 W kg^{-1} of power density, with an impressive long-cycle life of 96% retention after 8000 cycles. These findings underscore the potential of the coreshell CoS-0.4/MMO/rGO/NF nanostructure as an excellent electrode material for energy storage applications, offering valuable insights for further advancements in this field.

Namvar *et al*. [79] employed a microwave assisted method to produce leaf-shaped $MnMoO_4$ nanostructures, marking the first instance of such morphology synthesis. Moreover, through careful manipulation of solvent, power and irradiation duration, diverse shapes including spheres, rods and sheets were attained. Utilizing the leaf-like $MnMoO_4$ nanostructures as photocatalysts under ultraviolet light exposure, an impressive 88% degradation of methyl orange dye was achieved within 90 min. This study introduces an innovative, cost-effective and eco-friendly approach to synthesize $MnMoO_4$ nanostructures in various shapes and sizes, offering promising solutions for dye degradation in textile industry wastewater. Furthermore, Xu *et al*. [80] applied a one-step hydrothermal technique to prepare $MnMoO_4$ nanosheet array supported on nickel foam (NF@$MnMoO_4$) displaying exceptional electrochemical performance. This electrode demonstrated a remarkable specific capacitance of 4609 F g^{-1} at 1 A g^{-1}, maintaining a high capacitance of 2800 F g^{-1} even at 20 A g^{-1}. Impressively, the electrode retained 92.4% of its capacitance after 20,000 cycles, underscoring its outstanding cycle life. The NF@$MnMoO_4$ material's ultrathin and well-ordered channel structure facilitated abundant active sites on the surface and shortened ion transport paths, enhancing the redox reactions. Further, assembling an NF@$MnMoO_4$ //AC device yielded a high energy density of 107.38 Wh kg^{-1} at a power density of 801.34 W kg^{-1} and 72.18 Wh kg^{-1} at 3987.85 W kg^{-1}. Additionally, integrating the electrode with a commercial solar cell resulted in a self-charging integrated system displaying the potential of NF@$MnMoO_4$ for self-powered energy harvesting-storage applications. Similarly, Kim *et al*. [81] employed a simple sonochemical method to synthesize α-$MnMoO_4$ nanorods unveiling their high crystallinity through XRD analysis, Raman spectrum and HR-TEM studies. The electrochemical assessments, including CV and EIS measurements, indicated the pseudocapacitive behaviour of these nanorods. A significant specific capacitance of 168.32 F g^{-1} was achieved through galvanostatic charge-discharge analysis at a current density of 0.5 mA cm^{-2}. The α-$MnMoO_4$ nanorods exhibited an impressive capacitance retention of over 96%, thus highlighted their exceptional cyclability for supercapacitor applications.

Graphene-doped manganese molybdates: The photocatalytic activity of novel nitrogen-doped graphene coupled with metal molybdates (NG-$MMoO_4$) nanocomposites was also investigated to explore their prospective applications [82]. As a function of photocatalytic reaction time, a reduction in the methylene blue dye absorbance at distinctive absorption bands (290 and 660 nm) was observed. After combining 5 mg of NG-$MnMoO_4$, aliquots (5 mL) of aqueous methylene blue solution (20 mg L^{-1}) were mixed and the absorbance was monitored every 5 min. The results showed that in the presence of NG-$MnMoO_4$, the methylene blue absorption bands almost completely disappeared after 1 h. The photocatalytic efficiency of NG-$MnMoO_4$ was shown to be higher in a similar experiment with bare manganese molybdate as indicated by the change in methylene blue concentration (C_t/C_0) *vs*. exposure time. This comparison between bare manganese molybdate and the NG-$MnMoO_4$ nanocomposite demonstrated the superior photocatalytic activity of the former.

Cobalt molybdates: The $CoMoO_4$ nanoparticles were successfully synthesized through a sonochemical method without using surfactants and organic solvents as reported by Hajebi & Abedini [83]. The high purity of the as-prepared nanocrystalline sample was confirmed by XRD and EDS analyses. When utilized as photocatalyst, the as-prepared nanocrystalline $CoMoO_4$ demonstrated a methyl orange degradation of about 72% after 60 min of UV light irradiation. This result suggests that the obtained nanocrystalline $CoMoO_4$ is a favourable material with high potential for photocatalytic applications under ultraviolet light. The optical properties of the as-formed nanocrystalline products were also studied. Similarly, Yu *et al.* [84] also synthesized $CoMoO_4$ nanostructures effectively by annealing after a simple hydrothermal process. It is simple to convert the nanorods into nanosheets by varying the reaction temperature. It was observed that a particular 'contact surface' and suitable temperatures are necessary for the formation of $CoMoO_4$ nanosheet arrays. Furthermore, CM-140 electrode prepared at 140º C demonstrates the best electrochemical characteristics because of its unique chemical composition and appropriate nanostructure. At a power density of 685.8 W kg^{-1}, the alkaline CM-140/AC BSH device achieves a high energy density of 40 Wh kg^{-1}. After 5000 consecutive charge-discharge cycles, it exhibits outstanding cycling stability with an 86.9% capacitance retention rate. These findings point to this device's exciting potential for next-generation energy storage.

Using a new approach for the structural modification and enhancement of the inherent electrical properties of alternative electrode materials for electrochemical storage applications, Liu *et al.* [85] integrated the phosphorus atoms into P-$CoMoO_{4-x}$ nanosheets atop conductive Ni foam. The structural and electrical properties of P-$CoMoO_{4-x}$ were studied both theoretically and experimentally concerning the introduction of phosphorus and oxygen vacancies. The introduction of phosphorus into the lattice significantly enhances the redox reaction kinetics and electrochemical performance by reducing the Co–O bond energy and generating Mo species with lower oxidation states. Furthermore, the resulting 2D nanosheets, adorned with multiple nanoparticles, spontaneously assemble onto the conductive substrate. The enhanced P-$CoMoO_{4-x}$ material exhibits impressive rate capability and electrochemical stability, demonstrating a high specific capacity of 1368 C g^{-1} at a current density of 2 A g^{-1}. Moreover, an asymmetric P-$CoMoO_{4-x}$//AC supercapacitor configuration exhibits an exceptionally long cycle life (98.7% retention after 10,000 cycles at 10 A g^{-1}) and delivers superior energy densities of 58 and 18.8 W h kg^{-1} at power densities of 850 and 12,750 W kg^{-1}, respectively.

Metal-doped cobalt molybdates: Hybrid architectures comprising $Ni_3B/Ni(BO_2)_2@Ni_xCo_yMoO_4$ were successfully synthesized by integrating boronized $Ni_xCo_yMoO_4$ ultrathin nanosheets onto flexible carbon cloth substrates as reported by Zhao *et al*. [86]. By combining the beneficial properties of Ni_3B, $Ni(BO_2)_2$ and $Ni_xCo_yMoO_4$, these structures provide the improved conductivity and energy storage capacities. When operated at a high voltage of 1.7 V, the electrode material demonstrates an impressive capacity of 394.7 mAh g^{-1} at 1 A g^{-1}, a high specific capacitance of 370.7 F g^{-1} at 1 A g^{-1} (210 F g^{-1} at 10 A g^{-1}) in the hybrid supercapacitor. Moreover, the device exhibited consistent cycling performance, retaining 89% of its capacity after 5000 cycles and demonstrated a significant energy density of 131.8 W h kg^{-1} at a power density of 800 W kg^{-1} (maintaining 74.7 W h kg^{-1} at 8000 W kg^{-1}). This study contributes valuable insights into the utilization of boronized pseudo-capacitance materials, highlighting the potential applications of $Ni_3B/Ni(BO_2)_2@Ni_xCo_yMoO_4$ in future energy storage technologies.

GCN doped cobalt molybdates: A study was also conducted on the examination of novel graphitic carbon nitride/cobalt molybdate (g-$C_3N_4/CoMoO_4$) nanocomposites as photocatalyst for the efficient removal of doxycycline (DOX) from pharmaceutical industry wastewater in Izmir, Turkey [87]. The study found that the maximum 99% removal efficiency of DOX was achieved under specific conditions. The results also indicated the stability and effectiveness of the novel g-$C_3N_4/CoMoO_4$ nanocomposites photocatalyst in various environmental conditions and its potential for pharmaceutical wastewater treatment.

Copper molybdates: The potential of $CuMoO_4$ nanosheets grown on 3D nickel foam ($CuMoO_4$/NF) for supercapacitor applications was explored by Farahpour & Arvand [88]. The $CuMoO_4$/NF electrode exhibits impressive pseudocapacitive performance, boasting a high specific capacitance (2259.55 F g^{-1} at 1 A g^{-1}) and excellent cycling stability (only 10% capacitance loss after 5000 cycles). Furthermore, an asymmetric supercapacitor fabricated using $CuMoO_4$ nanosheets and activated carbon delivers a remarkable energy density (52.51 Wh kg^{-1} at a high power density of 600.11 W kg^{-1}) as reported by Seevakan *et al*. [89], which remains significant (16.87 Wh kg^{-1}), even at an ultra-high power density of 6.6 kW kg^{-1}. This combination of high-rate capability, cycling stability and minimal self-discharge positions $CuMoO_4$ nanosheets as a promising candidate for next-generation renewable energy storage devices.

Graphene-doped copper molybdates: Catalysts stimulate photosynthesis by recombining electrons and holes from visible light. Higher photocatalytic activity is associated with longer electron-hole separations. Thus, for the photocatalytic processes, the impact of GO inclusion in CuMo has also been studied. The GO-CuMo (1:2) nanocomposite has increased photocatalytic activity towards methylene blue degradation as reported by Singh *et al*. [90]. In 10 min, GO-CuMo (1:2) absorbed 30% of the initial concentration of methylene blue dye under dark conditions. while in 85 min, about 94% of the dye was broken down at a rate of 0.03 min^{-1}, which is faster than what was observed with pure CuMo. With a degradation rate of 0.045 min^{-1}, the whole breakdown of methylene blue in case of GO-CuMo (1:1) took about 70 min. The most rapid deterioration, almost 99%, had a photodegradation rate of 0.094 min^{-1} and was recorded using GO-CuMo (2:1). Furthermore, Kim *et al*. [91] prepared a supercapacitor device using a negative electrode made of reduced graphene oxide (rGO) and a positive electrode made of cobalt molybdate ($CoMoO_4$). This device achieved a low operating voltage of 1.5 volts, while also delivering high capacitance, energy density and power density. Moreover, the device showed excellent stability over a long charge-discharge test. Overall, the results suggest that this type of supercapacitor has great potential for future energy storage applications.

Silver molybdates: Under UV light illumination, the photocatalytic behaviour of Ag_2MoO_4 microparticles as produced was examined for the degradation of ciprofloxacin. The absorbance spectrum showed the gradual decay of ciprofloxacin, with several minor peaks and the primary absorption peak at 276 nm fading after 40 min. After 40 min, the relative intensity practically decreased, indicating that Ag_2MoO_4 microparticles caused 98% of ciprofloxacin degradation [92]. Recently, William *et al*. [93] reported a new, efficient method to prepare tiny, potato-shaped particles (nano-potatoes) made of a special material (β-Ag_2MoO_4) with mesopores (tiny holes). These nano-potatoes turned out to be great for storing energy in supercapacitors and could hold a lot of charge (2160 C g^{-1} at low power) and retained most of it (82%) even after repeated use (5000 cycles). The exceptional performance of this material is attributed to its rapid reactivity with the electrolyte and its distinctive capacity for energy storage. The researchers also built a supercapacitor using these nano-potatoes and found it delivered good energy storage (38.8% of its capacity) even when used at high power (7.6 kW kg^{-1}) and found to be stable, retaining 79.7% of its capacity after 5000 cycles.

Further indepth literature survey on the other metal based molybdate nano-crystalline materials, several researchers had carried out the significant novel materials with various shapes, sizes and architectures and their uses in the photocatalysis yielded a highly significant outcomes. Thus, the photocatalytic activity as well as the electrochemical performance of other metal molybdates are illustrated in Tables 1 and 2, respectively.

Conclusion

The review on molybdate-based nanocrystalline materials for energy sources and environmental remediation underscores their promising potential in addressing the critical challenges. These materials exhibit exceptional properties such as high surface area, excellent catalytic activity and structural stability, making them ideal candidates for various applications including energy conversion and environmental cleanup. Through a comprehensive analysis of recent advancements and research efforts, it is evident that molybdate-based nanocrystalline materials offer a viable pathway towards sustainable energy solutions and effective environmental remediation strategies. Continued exploration and optimization of these materials hold significant promise for addressing global energy needs and mitigating environmental pollution in the future.

TABLE-1
PHOTOCATALYTIC ACTIVITY OF METAL MOLYBDATES

Photocatalyst	Synthesis Method	Morphology	Photocatalytic activity	Ref.
α-$NiMoO_4$	Pechini	Nanospheres	Achieved 80% degradation of methylene blue (10 mg/L of solution/300 mL) within 2 h under visible light	[94]
$CoMoO_4$	Aqueous solution	Rods	Exhibited weak photocatalytic activity for methyl orange (5 × 10^{-6} M/100 mL) after 6 h under UV, visible and sunlight	[95]
α and β-$CoMoO_4$	Solution combustion	Irregular microplates	Attained 45% degradation of crystal violet (0.01 mmol dm^3/H_2O_2) within 90 min under UV light	[96]
$ZnMoO_4$	Bio-template directed hydrothermal	Hollow microspheres	Achieved 90% degradation of auramine O (25 moles per liter/200 mL) within 3 h under UV light	[97]
β-$ZnMoO_4$	Hydrothermal	Irregular plates	Yielded 53.2% degradation for violet blue R (VBR) after 36 h under visible light	[98]
β-$ZnMoO_4$	Hydrothermal	Irregular plates	Achieved 99.1% degradation for VBR (0.01 g/L/) and 88.6% for phenol after 84 and 96 h respectively under visible light	[99]
$ZnMoO_4$ monoclinic (50 mg)	Hydrothermal	Irregular polygonal plates	Achieved 100% degradation of methyl orange (10 mg/L of solution/50 mL) within 2 h under UV light	[100]
$Fe_2(MoO_4)_3$ (0.02 g)	Microwave-assisted hydrothermal	Pancakes	68% degradation of bromo pyrogallol red (0.01 g L^{-1}/25 mL) within 40 min under a 500 W Xenon lamp	[101]
$Fe_2(MoO_4)_3$/PS/HPPA (0.05 g)	Hydrothermal	Nanoparticles	Achieved 100% degradation of bisphenol A (BPA) (10 mg/L of solution) within 1 h under visible light	[102]
γ -Bi_2MoO_6 (0.05 g)	Vacuum-assisted nanocasting	Nanoplates	Achieved 82% degradation of rhodamine B (10-5 M/100 mL) within 5 h under visible light for five cycles	[103]
γ-Bi_2MoO_6 (0.2 g L^{-1})	Template-free solvothermal	Nanowires	Achieved 82% degradation of bisphenol A (10 mg/L of solution/50 mL) and 81% degradation of carbamazepine (2.5 mgL-1/50 mL) within 40 and 50 min respectively under sunlight	[104]
γ-Bi_2MoO_6 (0.05 g)	Hard template	Hollow spheres	Achieved 92% degradation of tetracycline (10 mgL^{-1}/50 mL) within 90 min under light	[105]
γ-Bi_2MoO_6 (0.1 g)	Template-free solvothermal	Cage-hollow spheres	Achieved 90% degradation of phenol (20 mg/L of solution/100 mL) within 8 h under visible light	[106]
Bi_2MoO_6 Koechlinite (0.2 g)	Solvothermal	Nanosheets and microspheres	Achieved 100% degradation of rhodamine B (10-5 M/200 mL/H_2O_2) within 20 min under sunlight	[107]
γ-Bi_2MoO_6 (0.05 g)	Template-free solvothermal	Plates	Achieved 91% degradation of Congo red, 45% degradation of reactive red 141, 85% degradation of ofloxacin and 70% degradation of norfloxacin (all at 10 mg/L of solution/200 mL) within 4 h under visible light for five cycles	[108]
Bi_2MoO_6 Koechlinite (0.05 g)	Solvothermal	3D spheres	Achieved 90% degradation of tetracycline (30 mg/L of solution50 mL) within 150 min under UV light	[109]
PAN/γ-Bi_2MoO_6 (0.05 g)	Solvothermal	Microtubes and nanofibers	Achieved 2% degradation of rhodamine B (10 mg/L of solution/100 mL) within 3 h under visible light	[110]

TABLE-2
ELECTROCHEMICAL PERFORMANCE OF METAL MOLYBDATES

Metal molybdates	Method	Specific capacitance	Ref.
KCu_7S_4@$NiMoO_4$	Hydrothermal	The KCu_7S_4@$NiMoO_4$ electrode exhibits a superior specific capacity of 1194.6 Fg^{-1}, with a retention rate of 92.3%. When utilized in an ASC device, it showcases an ultrahigh energy density of 55.9 Wh/kg. Notably, even after 10,000 cycles, it maintains remarkable cycle stability, retaining 91.3% of its capacitance	[111]
$CoMoO_4/MnO_2$	Hydrothermal	The composite electrode comprising $CoMoO_4/MnO_2$ showcased outstanding rate capability at 60.3% and achieved a notable areal capacitance of 2.27 F cm^{-2} at a current density of 1 mA cm^{-2}	[112]
Su-GC@$MnMoO_4$	Hydrothermal	The electrode material (GC@$MnMoO_4$) exhibited exceptional performance in supercapacitors, showcasing a high capacitance of 528 Fg^{-1}, even under fast charge/discharge rates of 2 Ag^{-1}. Impressively, it retained nearly all its capacitance (98.7%) after undergoing thousands of charging cycles (5000). When integrated into a full supercapacitor device, researchers achieved a balanced energy storage of 35.4 Wh kg^{-1} and power delivery of 223 W kg^{-1}. Furthermore, the device maintained a high capacitance retention rate of 96.7% over a significant number of cycles (10,000).	[113]
$CoMoO_4/CoMoO_4$	Hydrothermal	Binder-free electrodes employing hierarchical $CoMoO_4/CoMoO_4$ core/shell nanostructures with a dandelion-like morphology showcase remarkable pseudocapacitive behaviour. They achieve a high specific capacitance of 1548 Fg^{-1} at a current density of 1 Ag^{-1}. Furthermore, they demonstrate impressive rate capability, retaining 69.3% of their capacitance even at a high current density of 13 Ag^{-1}. Additionally, these electrodes exhibit outstanding cycling stability, maintaining 94% of their capacitance after undergoing 5,000 charging and discharging cycles at 8 Ag^{-1}.	[114]
$NiMoO_4$@Mg-Co(OH)F	Hydrothermal	NM-MCF nanocomposite electrode that has been improved exhibits exceptional capacitive performance. It can sustain a remarkable 86% capacity retention after 6000 cycles and has a specific capacitance of 1630 Fg^{-1} at 1 Ag^{-1}. NM-MCF is particularly noteworthy for its stable rate capacity, reaching 56.5% from 1 to 15 Ag^{-1}, which is higher than that of Mg-Co(OH)F (28.8%) and $NiMoO_4$ (56.4%). A hybrid capacitor device is constructed with NM-MCF composites as the positive electrode and activated carbon as the negative electrode. It exhibits remarkable maximum energy and power densities of 28.2 Wh kg^{-1} and 0.7 kW kg^{-1} respectively, as well as an exceptional long-term stability of 73.3% retention upon 6000 cycles.	[115]
PDA-rGO@$NiMoO_4$	Hydrothermal	The composite material exhibited a specific capacitance of 856 F g^{-1} (514 Cg^{-1}) at a current density of 1 Ag^{-1}. In contrast, an asymmetric supercapacitor employing activated carbon achieved an energy density of 48 $Whkg^{-1}$ at a power density of 800 Wkg^{-1}. Following 5,000 cycles of charging and discharging, a retention rate of 73% capacitance was attained.	[116]
$MnMoO_4{\cdot}H_2O/Ni_3S_2$	Hydrothermal	$MnMoO_4{\cdot}H_2O$ and Ni_3S_2 electrodes with a hierarchical structure perform well electrochemically. At 1 Ag^{-1}, the MMONS electrode has an exceptional specific capacity of 1136 Cg^{-1} and extraordinary cycle stability, holding onto 77.4% capacitance even after 10,000 charge–discharge cycles at 5 Ag^{-1}. The device, when configured as an asymmetric supercapacitor (ASC), attains an energy density of 55.87 Wh kg^{-1} at 695.97 Wkg^{-1}, demonstrating remarkable cycle stability and retaining 85.5% capacitance after 5000 cycles.	[117]
$NiMoO_4$/NiCo-LDH	Hydrothermal	The $NiMoO_4$/NiCo-LDH nanocomposite displays a significant specific capacity of 153.7 mAh g^{-1} at 1 Ag^{-1}, attributed to the behaviour of its $NiMoO_4$ core during charge/discharge cycles, which enhances cyclic stability. Furthermore, when utilized as the positive electrode in an asymmetric supercapacitor (ASC) paired with activated carbon derived from horsetail trees (AHTC), it achieves a commendable energy density of 40.3 Wh kg^{-1} at 425.5 Wkg^{-1}, demonstrating impressive cycle performance.	[118]
$CoMoO_4$@NCS	Hydrothermal	The $CoMoO_4$ @NCS composites demonstrate a significantly enhanced specific capacitance of 1276 Fg^{-1} at 0.5 Ag^{-1}, which is double that of pristine $CoMoO_4$ nanorods (604 Fg^{-1}). Furthermore, these composites exhibit exceptional cycling performance, maintaining 98% of their specific capacitance after 7000 cycles at 1 Ag^{-1}. Additionally, the asymmetric supercapacitor ($CoMoO_4$ @NCS//AC) device achieves a notable energy density of 48.3 Wh kg^{-1}. Impressively, this fabricated device displays outstanding stability, with only a 4% capacitance loss rate after 10,000 cycles.	[119]
$g\text{-}C_3N_4$@$NiMoO_4$/$CoMoO_4$(gCN@NCM)	Hydrothermal	The gCN@NCM composite showcased remarkable electrochemical performance, featuring a high specific capacitance of 641.5 F/g and exceptional cycle stability with only a 15.79% decrease in capacitance after 8000 cycles. Additionally, the specific capacitance of the gCN@NCM//active carbon (AC) device saw a 30% enhancement within the initial 2000 cycles, while maintaining 110% of its original specific capacitance even after 10,000 cycles.	[120]
$FeMoO_4$ nanoparticles	Hydrothermal	β-$FeMoO_4$ reveals remarkable specific capacitance of 600 Fg^{-1} at 5 Ag^{-1}, The material exhibits mixed surface capacitive-pseudocapacitive mechanism. The Ni-Cu-P//β-$FeMoO_4$ supercapacitor showed a specific energy of 40.75 Wh Kg^{-1}. The device showed exceptional stability over 12,000 charging/discharging cycles.	[121]

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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