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Powering the future: emerging role and mechanistic insights of polyoxometalates in piezo- and triboelectric energy materials

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In recent years, the design of advanced piezoelectric and triboelectric nanogenerators (PENGs and TENGs) has gained significant momentum as a sustainable strategy for harvesting mechanical energy from the environment. A central approach to improve their performance involves the incorporation of functional fillers into host matrices, enabling enhancement of charge transport, dielectric properties, and interfacial stability. While numerous studies have focused on organic and inorganic fillers, polyoxometalates (POMs) remain an underexplored yet exceptionally promising class of multifunctional components. POMs exhibit unique structural diversity, highly tunable redox chemistry, strong electron-accepting ability, and rich opportunities for chemical modification, making them versatile platforms for tailoring energy conversion processes. This review provides a comprehensive discussion of recent progress in integrating POMs into piezoelectric and triboelectric materials, including ceramics, polymers, and composite systems. We highlight mechanistic insights into how variations in POM composition, heteroatoms, addenda atoms, counter-cations, and framework architectures influence dielectric response, electron transfer, and energy-harvesting efficiency. Furthermore, emphasis is placed on structure–property–performance correlations, revealing how rational design of POM-based fillers can yield NGs with higher output power, improved durability, and multifunctional capabilities. Beyond material optimization, POMs also open pathways for designing next-generation energy devices that exploit synergistic piezo-triboelectric effects, offering potential for self-powered electronics, wearable sensors, and green energy technologies. Overall, the review underscores the transformative role of POM-based fillers in advancing the frontiers of energy harvesting. By outlining future research opportunities, it aims to guide the development of innovative POM-enabled NGs for sustainable and scalable applications.

1. General aspect

The increase in the world's population, the growing energy demand, and depletion of fossil fuel resources have drawn researchers' attention to new energy sources. Additionally, considering global warming and environmental pollution, there is a greater need to design and develop energy conversion devices to reduce the use of fossil fuels. Excessive consumption of fossil fuels has posed many risks to the economy and the environment. Therefore, the idea of producing renewable and green energy has become the focus of researchers and has attracted extensive research in this field. The development of various methods for conversion, harvesting, and storage based on renewable energies can be carried out with different strategies including batteries, solar cells, nanogeneratores (NGs), photovoltaic and electrochemical devices. Among them, the conversion of mechanical, frictional, electromagnetic, and inductive energies into electrical energy has attracted the attention of many scientists over the past twenty years. Energies resulting from body movements, raindrop, thermal energy, wind, vehicles, industrial machines, construction, *etc.*, which exist in our surroundings and are wasted, can be converted and stored as electrical power.[1] For this purpose, piezo-, tribo- and pyroelectric transduction mechanisms have been proposed. The integration of two devices, energy harvesting and energy storage, can help achieve a self-powered system and has many large-scale applications. Specially, the design and construction of such a device can serve as a suitable replacement for batteries, which create significant pollution in the environment. They will also be used in portable wearable, electronic transport vehicles, and health monitoring systems.[2–4] Such integrations for solar cells, NGs, and fuel cells with supercapacitors or batteries have been studied before.[5–7] From a broader perspective, the design and fabrication of an intrinsically integrated device that can simultaneously harvest, convert, and store

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energy in a single device take precedence over extrinsic integrated devices.[8]

After the development of such devices, researchers, became interested in the advantages of piezo- and triboelectric materials, including rapid response, flexible structure, miniaturized size, low energy consumption, and high resolution,[4] which will be described in more detail in the next sections.

1.1. Piezoelectricity

The piezoelectric effect was discovered by Curie brothers, Jacques and Pierre in 1880.[9] The term "piezoelectricity" comes from the Greek word piezein ('to press') and ēlektron ('amber', the origin of the word electricity, since rubbing amber was the first known source of static electricity), together describing electricity generated by mechanical stress.[10] The piezoelectric effect refers to the ability of certain materials to convert mechanical energy generate from external pressure into electrical energy.[11] Later, the Curie brothers discovered that applying an electric field to quartz crystals causes their deformation. This phenomenon, predicted in 1881 was named the converse piezoelectric effect.

Piezoelectricity is based on the non-centrosymmetric distribution of positive and negative charges in the unit cell of a material.[12,13] Due to the stress or mechanical vibration, the dipole moment of the unit cell changes, which subsequently generates an electric charge.[14,15] Quartz is a nonpolar crystal that does not have a net electric net dipole in the absence of stress. However, when stressed, charge separation induces a piezoelectric potential.[16–21] But some piezoelectric materials, like zinc oxide, with polar crystals exhibit a polarization even in a zero-stress state due to separation between positive and negative charges.[22,23] Since the polarization of ferroelectric materials changes under stress, all ferroelectric materials potentially exhibit piezoelectric properties.[24–27] It should be noted that piezoelectric effects were first studied in nonsymmetric crystals and later extended to ceramic materials which have polarization structure based on their atoms and the way the crystal are formed. Different polar axes appear in polycrystalline materials but all dipoles lie in one direction in polarized nanocrystals Fig. 1.[28–30]

However, the first industrial application of the piezoelectric effect began in the 1950s, and thereafter it was widely used in various topics and instruments such as sensors, transducers, actuators, *etc.* (Fig. 2).[31] Distribution of published articles based on topic of piezoelectricity since the year of first report in 2006 is presented as Fig. 3.

First report of a piezoelectric nanogenerator (PENG) was in 2006 by Wang.[32] NGs have gained increasing attention (Fig. 4a) by focusing on the different design, different materials, compact and small size, portable and environmentally benign devices.[33–38] Totally, since 2006 when the first PENG was reported, 2309 articles related to PENGs have been published, and their distribution in various fields is shown in Fig. 4b. Based on Scopus data, "Materials science" is the most important field.

1.2. Triboelectricity

Triboelectricity relies on generating a charge due to the friction between two contact surfaces or inducing a charge by bringing surfaces close together. The triboelectric effect arises when two materials come into contact and electrons transfer from one surface to the other, leading to static electricity buildup upon separation. The effect is common when objects are rubbed together, but the underlying mechanism involves complex interactions at the atomic level, especially involving electron transfer, chemical bonding, and surface morphology. The direction of electron flow depends on the materials' electron affinities, as described by the triboelectric series. In the triboelectric series, materials are ranked by their tendency to lose electrons and become positively charged (*e.g.*, glass, wool, nylon) or to gain electrons and become negatively charged (*e.g.*, PTFE, silicone, PVC).

Upon separation, some atoms retain the extra electrons and some lose them, resulting in net surface charges. The charge transfer occurs mainly due to differences in work functions (energy needed to remove electrons from a solid), local atomic environments, and sometimes molecular exchange. For insulators (where charges cannot immediately flow away), this charge imbalance persists, manifesting as static electricity. The effect is influenced by surface roughness, environmental conditions, and particle velocity.

Main mechanism of charge transfer in triboelectricity is not explained by a single phenomenon. Multiple mechanisms are working together including electron transfer, ion transfer, molecular adsorption, chemical bonding and surface states, trapped charges, and defects. When two surfaces touch, electrons move from the material with lower work function (weaker electron binding) to the one with higher work function (stronger electron affinity). After separation, the donor material becomes positively charged, and the acceptor becomes negatively

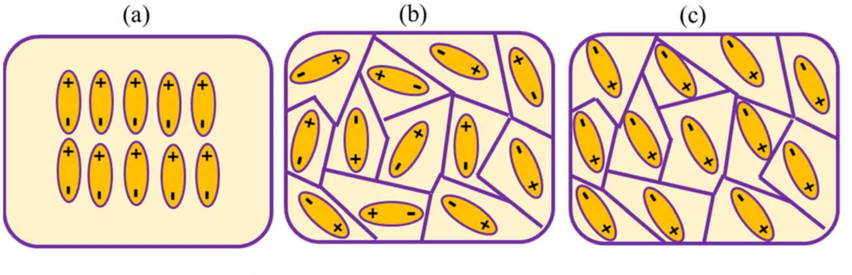

Fig. 1 Dipole arrangement in (a) mono-crystalline; (b) nonpolarized poly-crystalline; (c) polarized poly-crystalline materials.

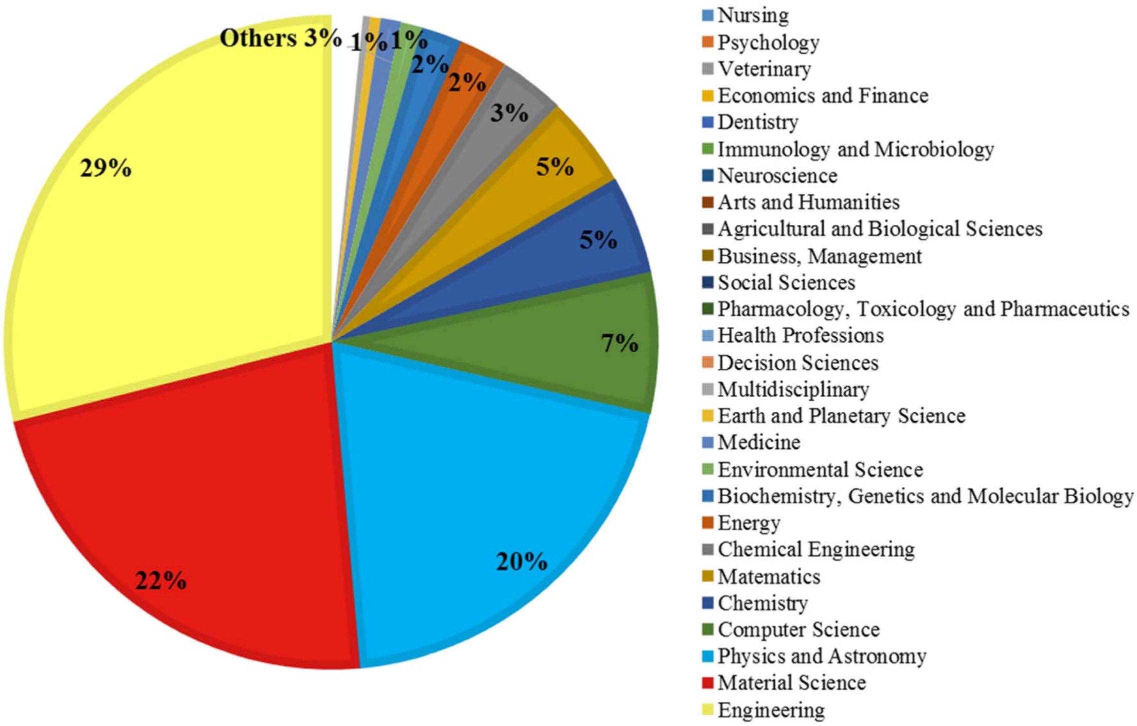

Fig. 2 Distribution of published papers related to piezoelectricity based on subject area (extracted from Scopus, 2/27/2025).

charged. Surfaces are rarely pure, water or ions are adsorbed and contraction can cause migration of these ions between surfaces. This mechanism is especially important in humid or chemically active environments. By surfaces touching atomic orbitals overlapped and forming temporary bonds. By surface separation, some bonds breaking and leaving dangling bonds leading to unpaired charges. Insulators can trap charges in defect or localized electronic states and during contraction leading to long-lasting static charges.

Based on the combined effect of contact electrification and electrostatic induction, triboelectric nanogenerators (TENGs) are regarded as sustainable energy harvesting devices.[39–41] TENGs have high output power and conversion efficiency in addition to all the benefits of PENGs. It necessitates cleverly designing multiple ways to induce and enhancing surface contact electrification.[42] TENGs can convert low frequency and small-amplitude mechanical energy into high-value electricity result in widespread since it was invented by Wang *et al.* in 2012.[43] Considering that there are many mechanical vibration in our surroundings that are waste energies, TENGs has become one of the most promising candidates for the expansion of renewable energies. After that, many researchers tried to improve its efficiency by choosing suitable materials, controlling morphology, and designing different NGs by optimization

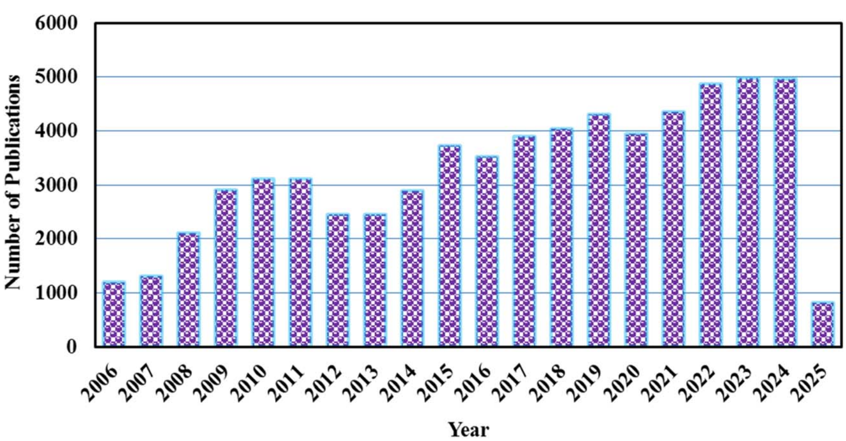

Fig. 3 Distribution of published articles based on topic of piezoelectricity since the year of first report in 2006 (extracted from Scopus, 2/27/2025).

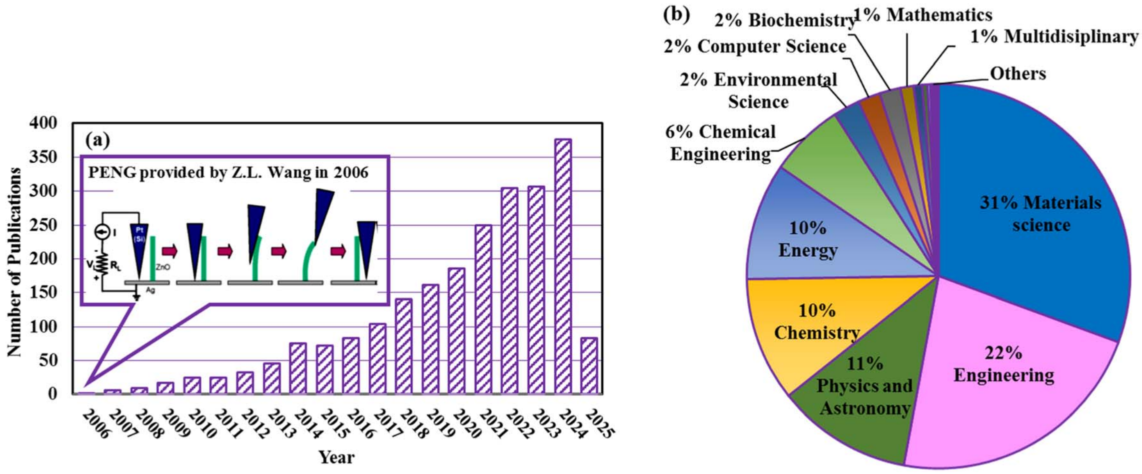

Fig. 4 (a) Number of publications on PENGs; (b) distribution of published articles on PENG's subject area since 2006 (extracted from Scopus, 2/27/2025).

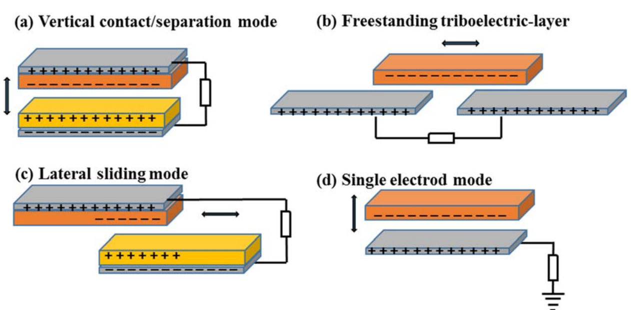

Fig. 5 Schematic illustration of the four fundamental working modes of TENGs (a–d).

of production conditions.[44–51] Factors like material pair selection, environmental humidity, and physical surface state affect triboelectric output. Choosing suitable materials is still the most effective way, and developing a novel materials is of great significance for TENGs and also PENGs.

TENGs can operate in four fundamental modes, each determined by the way surfaces interact and generate charge (Fig. 5). The vertical contact–separation mode generates charge flow as two layers repeatedly touch and separate. In the lateral sliding mode, in-plane motion between surfaces enables continuous charge transfer. The single-electrode mode allows one triboelectric surface to move freely while a single electrode connects to the ground, enabling simpler device structures for wearable and environmental applications. Finally, in the freestanding mode, a mobile triboelectric layer shifts between fixed electrodes, driving charge redistribution. These modes offer adaptable strategies for harvesting energy from vibrations, human motion, wind, or water waves.

2. Materials

Various piezoelectric materials have been used for PENGs fabrication, including crystals (quartz, lithium niobate, Rochelle salt), ceramics (barium titanate, lead-zirconate-titanate), polymers (polylactic acids (PLA), polyvinylidene fluoride (PVDF), cellulose derivatives), composites (PVDF-ZnO, cellulose-$BaTiO_3$, polyamides-PZT), and bioinspired materials.[52] On the other hand, there are also various types of piezoelectric materials from natural sources.[53] Organic materials generally have poor thermal stability, thus despite some of them having high electrical output, they are less suitable. In addition, four types of TENGs have been introduced: organic–organic[54] organic–metal[55] organic–semiconductor[56] and metal–semiconductor systems.[57] Researchers tend to design TENGs and PENGs using fillers that not only enhance the thermal stability of organic materials but also possess high transfer and storage capabilities.[58] The impact of incorporating organic and inorganic components on piezo or tribo properties is very important and should be carefully considered. Among different materials,[59–63] polyoxometalate (POM), as an outstanding class of tunable and redox-active materials, can be used in TENGs and PENGs due to their weather resistance, durable chemical corrosion resistance, high thermal stability, good electron transfer and charge storage abilities and good chemical stability.[64]

Although many articles and review articles have been published on natural or synthetic materials for PENG or TENG fabrication, the number of articles that have used POMs is very limited. Therefore, this article focuses on reports that have utilized these compounds in various structures. Along with the main issues and challenges, the current state of the art and the prospects for POM-based PENGs and TENGs are covered here.

2.1. Polyoxometalates

POMs represent a class of anionic metal-oxo clusters that are built from the connection of $\{MO_x\}$ polyhedra, consisting of M as high valent transition metal.[65] The history of POMs, according to some opinions, dates back to 1783 when Scheele and co-workers were studying reduced molybdenum salts.[66] However, the yellow precipitate of ammonium phosphomolybdate was

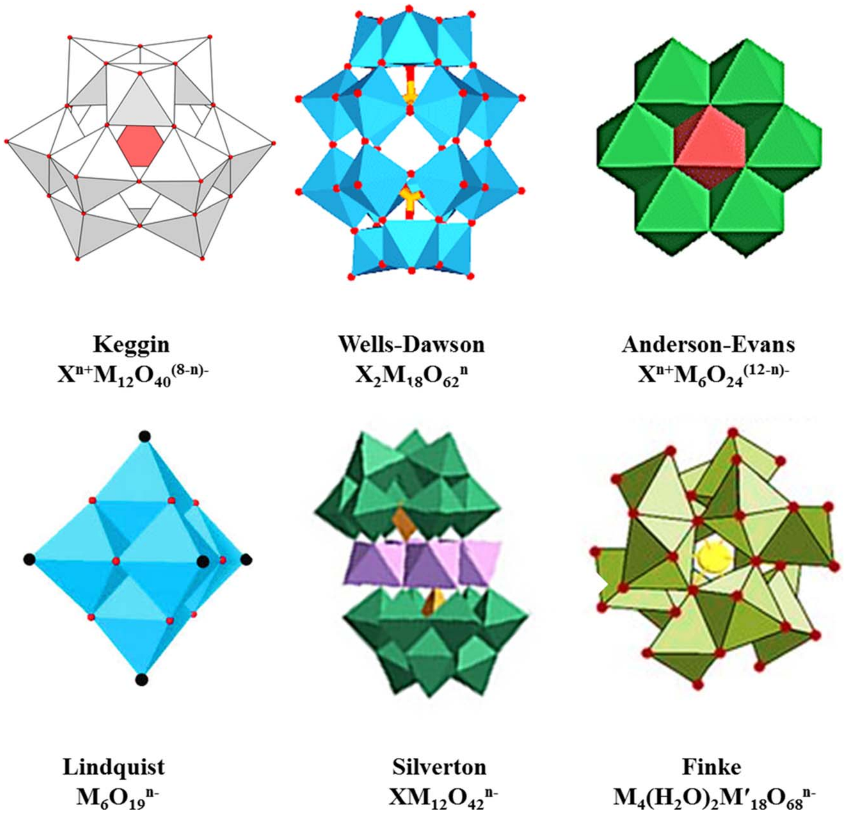

Fig. 6 Most important structures of POMs.

synthesized and introduced by Berzelius in 1826.[67] In 1934, Keggin introduced the $H_3PW_{12}O_{40}\cdot 29H_2O$ (PW) structure using X-ray diffraction measurements, and such structures were subsequently named Keggin structures.[68] Nowadays, with the advancement of materials science and nanotechnology, POMs continue to be very useful materials that many researchers are working on their synthesis, characterization, and applications.

POMs are classified into two main classes: (i) isopolyoxo anions (IPA) with the general formula of $[M_mO_y]^{p-}$, M called as the addenda atom. (ii) Heteropolyoxo anions (HPA) with the general formula of $[X_xM_mO_y]^{q-}$, where X is called the hetero-atom and is present in smaller proportion compare to the addenda atoms. Commonly, IPA are much more unstable than their HPA counterparts.[66] Addenda atoms are commonly Mo, W, V, Nb, *etc.* in their highest oxidation states (d^0, d^1) and hetero atoms are being P^{5+}, Si^{4+}, Co^{3+}, B^{3+}, *etc.*

Numerous review articles have been written about POMs and their applications, in which various properties and structures have been discussed.[69–73] In this review, the main focus will be restricted to application of POMs in the construction of PENGs and TENGs as well as their mechanisms in improving PENG and TENG performance, which are among the latest application for POMs. Thus, the so-called Keggin, Wells–Dawson, Anderson–Evans, Silverton, Finke and Lindqvist POMs, as six distinct structural families, will receive special attention (Fig. 6). Also, Keplerate-types with icosahedral symmetry, named after J. Kepler for their structure based on the stellating of a dodecahedron will be discussed. These structures are essentially large, hollow POM capsules with a diameter of 2.5 to 2.9 nm. Their electronic structure resembles that of solids rather than discrete molecules.

The Keggin structure, the most popular structure for HPAs, has a central tetrahedron consisting of X surrounded by four trimetallic groups. The Well–Dawson structure, is an HPA with the general formula $[X_2M_{18}O_{62}]^{q-}$, which produced by connecting two Keggin units by a shared corner. Each Keggin unite

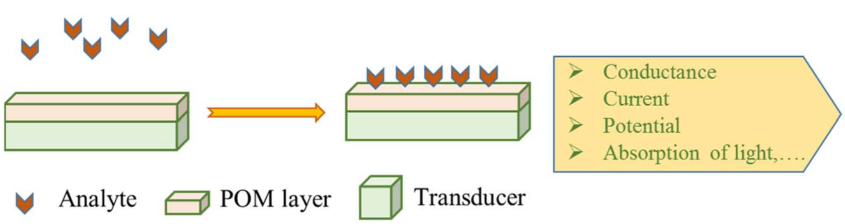

Fig. 7 Schematic of the POM-based sensor composition and measured signal.

cluster has lost a $\{M_3O_{13}\}$ group. The Anderson-Evans structure is an HPA with the formula of $[XM_6O_{24}]^{q-}$, where six edge-sharing octahedra are arranged into a planar hexagon around the X atom. The Lindqvist structure is an IPA with the formula $[M_6O_{19}]^{p-}$ consisting of an octahedral arrangement.

Also, by hydrolytically eliminating one or more metal sites from Keggin or Dawson structures, another kind of POMs is synthesized from the primary structures. Vacancies of lacunary structures can be linked to other metal, non-metal atoms or organic to modify the structure or the properties of POMs.[74–77]

Our research group has demonstrated that POMs possess excellent electron-transfer capabilities. Many researchers have used these compounds in photovoltaic systems,[78] electronic devices,[79] perovskite photodetectors,[80] electrochromic smart windows,[81] dye-sensitized solar cells,[82] and photocurrent response applications.[83] POMs have variable energy levels, and their bandgaps can be matched with those of semiconductors. In such cases, POMs act as strong electron acceptor and easily accept electrons from the conduction band of the semiconductor. Additionally, POMs have reversible redox properties, making these materials suitable media for electron transport.[84–87]

The ability of POMs to be functionalized by integrating with various metals, providing versatility for forming compounds with diverse redox properties and the capability to transfer one or multiple electrons, makes POMs highly noteworthy. Also, many active sites, structural diversity and electronic regulation are provided by this functionalization. The redox properties of some of these compounds allow reversible absorption of sometimes more than 20 electrons per cluster unit.[88–91] Additionally, by selecting one or more suitable metals in their structure, their redox potential and electron storage capability can be adjusted and tuned chemically according to needs.

The fabrication of POM-based composites can also enhance their properties, and the resulting nanocomposites can be used in a wide range of applications. For example, the fabrication of POM-based nanocarbon composites can enhance their electronic conductivity. Alternatively, POM-based polymer composites improve their conductivity, flexibility, and ease of manufacturing process. Additionally, metal organic frameworks form composite with POMs and produced nanocomposites that increase the surface area of POMs, create more active sites, and enhance their stability. Moreover, POMs are candidates for applications in covalent/coordination design of mixed organic–inorganic frameworks.[92] Thus, composite materials made from two or more components including POMs can create new compounds with unique functionalities[77,93–96] Because POMs resist structural degradation under oxidative, reductive, and acidic conditions, they are widely used and help materials last longer. Resultant composites have shown promise as effective materials for energy storage, energy conversion, sensors, and fuel cells based on these benefits.[94,95,97]

3. POMs based PENGs/TENGs

First of all, Gomes and co-authors wrote a review based on POM functionalized sensor.[98] An overview of POM structures utilized in electrochemical, optical, and piezoelectric sensors was provided in this article (Fig. 7). Transduction could be voltammetric, amperometric, potentiometric or conductometric (electrochemical), absorbance, reflectance, luminescence (optical) or mass and acoustic properties (piezoelectric). However, only one paragraph was dedicated to the piezoelectric application of POMs.

They explained about quartz crystal microbalances (QCM) sensors which were used to investigate the adsorption of Keggin PW onto a copolymer-coated QCM.[99] Additionally, they used $(NBu_4)_3[PW_{11}O_{39}\{(SiC_6H_4NH_2)_2O\}]$, an organic-inorganic hybrid POM to fabricate a sensor for benzo[*a*]pirene detection.[100] It appears that, the presence of amine groups increases biosensor sensitivity.

An acoustic wave sensor coated with the Keggin type $[PMo_{10}V_2O_{40}]^{5-}$ was reported by Verissimo *et al.*,[101] which detected hydroxymethylfurfural as a carcinogenic and genotoxic material in honey. They compared the results of their new methodology with the conventional spectrophotometric method and found its quantification limit was well below the legislation threshold. They also used a hybrid POM containing Mn(III), $[(C_4H_{90}N)]_4[PW_{11}MnO_{39}]$, as a sensitive membrane of the piezoelectric quartz crystal demonstrating good stability for acetaldehyde detection.[102]

He *et al.* propose inexpensive, flexible and transparent PENGs using POMs with various compositions and structures including $XM_{12}O_{40}{}^{m-}$ (where X = P, Si, and M = Mo, W) and two

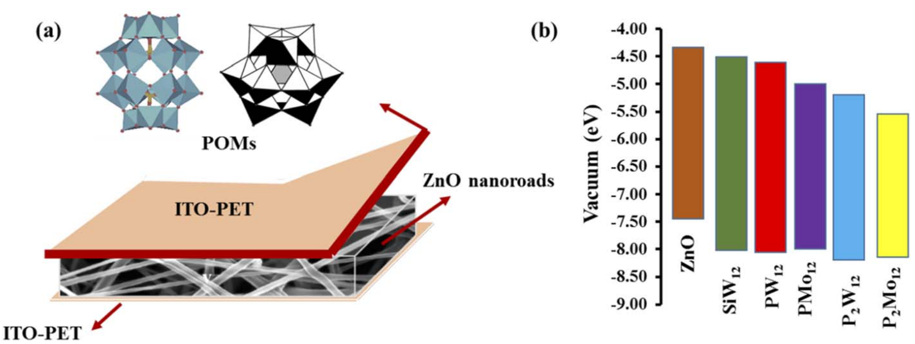

Fig. 8 (a) Schematic of the flexible device POM-based PENG; (b) LUMO (Lowest Unoccupied Molecular Orbital) and HOMO (Highest Occupied Molecular Orbital) energy levels *vs.* vacuum for POMs used in this study as well as ZnO.

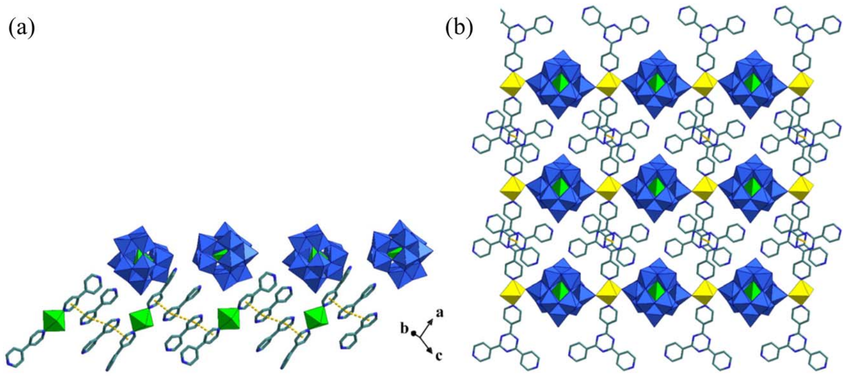

Fig. 9 (a) 1D supramolecular network of A; (b) 1D supramolecular network of B. Free solvent molecules and hydrogen atoms were omitted for clarity. Color code: WO_6, light blue octahedral (for a); ZnO_4 (for a and b) and ZnN_2O_4 (for a), bright green octahedral; CuN_2O_4, yellow octahedral (for b); C, grey; N, blue, reproduced from ref. 50 with permission from Royal Society of Chemistry, copyright 2025.

Dawson POMs ($X_2M_{18}O_{62}{}^{n-}$ (where X = P and M = Mo, W)). These composites were selected as the top electrodes to evaluate their effect on the output performance of NG.[78] The good solubility of these POMs in methanol for spin coating, the stability of these compounds after redox reactions, and their low visible light absorption were the main reasons for this selection (Fig. 8a).

The LUMO energy levels of POMs depend on their coordination atoms, which can affect their reduction tendency. According to Fig. 8b the addenda atoms obtain electrons from ZnO nanorods and are reduced. Results showed a stronger tendency for electron injection exist in Dowson-type compare with Keggin structures when the same hetero- and addenda atoms are used. These evidences indicate that the output performance of Dawson POMs is superior to that of Keggin POMs. Due to the transparency of these PENGs, they are appropriate candidates for windows applications.

Following these investigations and the obtained results, it was predicted that POMs could serve as electron transfer compounds to improve triboelectric properties, simultaneously enhancing electron transfer characteristics and charge storage capacity. Therefore, a metal–semiconductor TENG titanium oxide –based film modified with POMs was prepared, with a thin film of metals such as silver, copper, and aluminum used as the friction component.[56] The electrical output of TENGs designed with different polymers varies, and is dependent on the energy levels between the LUMO of the POM and the conduction band of TiO_2, such that a greater difference between them leads to a higher tendency for electron transport to the POM. They synthesized POMs/TiO_2 film through a layer-by-layer method.

The best energy level matching was obtained by Ag, followed by Al, and then Cu. In the presence of POMs, the energy levels demonstrated better alignment with TiO_2. The electrical output for different TENGs modified by POMs has been examined as $K_6P_2Mo_{18}O_{62}$ > $H_3PMo_{12}O_{40}$ > $H_4SiMo_{12}O_{40}$ > $K_6P_2W_{18}O_{62}$ > $H_3PW_{12}O_{40}$ > $H_4SiW_{12}O_{40}$ and short circuit current (I_{SC}) for $K_6P_2Mo_{18}O_{62}$ was 20 nA. The results of the study have shown that Dawson structures are better than Keggin ones, and also, POMs containing molybdenum are better than those containing tungsten. The authors describe the working mechanism of designed TENGs.[56]

Zhang *et al.* synthesized two α-Keggin-type POM-based metal organic hybrid compounds with zero and one dimensional infinite chain structures[50] and used them as TENGs. The Results showed an output performance of 395 V, 34.8 μA with high stability. The hybrid compounds were $(4,4'\text{-}H_2bpy)_2[Zn(4,4'\text{-}bpy)_2(H_2O)_4][ZnW_{12}O_{40}]\cdot 4H_2O$ (A) and $[Cu(H_2TPT)_2(H_2O)_2(ZnW_{12}O_{40})]$ (B), (with 4,4′-bpy: 4,4′-bipyridine and TPT: 2,4,6-tri(4-pyridyl)-1,3,5-triazine) (Fig. 9). Zn^{2+}/Cu^{2+} ions serve as bridges in these structures to construct POM-containing inorganic–organic hybrid compounds, resulting in two hybrids: one one-dimensional chain infinite architecture and another zero-dimensional discrete architecture. In these TENGs, PVDF was used as the opposite friction layers. TENG fabricated with the hybrid material showed good stability and was able to rapidly power 2046 LEDs.

G. Giancane *et al.* designed a novel interfacial layered blend by an organic–inorganic heterojunction including POM-bis-pyrene (pyrPOM) as a receptors binding fullerene-based acceptors and in particular the most used phenyl-C61-butyric acid methyl ester (PCBM).[103] They used a di-vacant Keggin-type decatungstosilicate bisfunctionalized with pyrene and PCBM (pyrPOM@PCBM) Fig. 10. Piezoelectric properties of the pyrPOM@PCBM film was studied. Their research revealed that benefits were further enhanced when an external bias was used to polarize the interlayer, resulting in an increase in open-circuit voltage (V_{OC}) of up to 34% when compared to the traditional donor/acceptor configuration.

The potential for using POM and reduced graphene oxide (RGO) as nanofillers to improve the piezoelectric performance of PVDF nanofibers was explored by our research group.[104] When nanofibers were synthesized using the electrospinning technique, the molecular dipoles within the nanofibers aligned, facilitating stretching and polarization. In this study $[(tert\text{-}Bu)_4N]_4PCoW_{11}O_{39}$ as an organic-inorganic hybrid POM was utilized (Fig. 11). The addition of organic cations imparted semi-conducting qualities, significantly enhancing the salt's

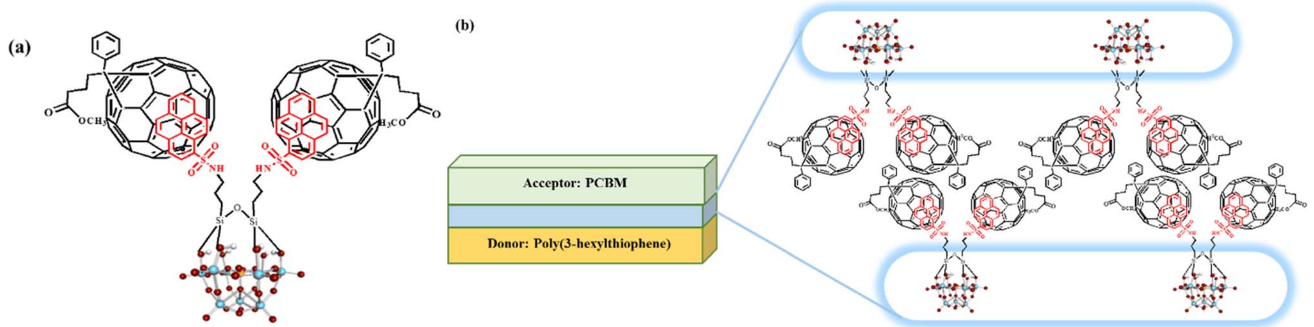

Fig. 10 (a and b) Stacking layers configuration of POM-bis-pyrene as a receptor binding fullerene-based acceptor and phenyl-C61-butyric acid methyl ester.

electrical conductivity. Findings demonstrated that, compared to PVDF PENG, the electroactive phase and electron transport properties were greatly improved. In the realm of flexible and wearable electronics, PENGs based on POMs, particularly those that incorporate organic cations, are considered to have significant potential. Previous work by our group employed tungsten and cobalt based POMs in selective organic processes because of their electron-donating and electron-accepting abilities.[105–107] Results showed that Co-containing POMs are excellent electron transporting compounds, suitable for ionic interactions and a variety of transformations. Furthermore, by creating microcapacitors inside the polymer matrix, conductive fillers enhance electrical and mechanical properties while stabilizing the β phase. These fillers raise power conversion efficiency of PVDF's in energy harvesting applications. With its large surface area, two-dimensional structure, and outstanding electrical conductivity, RGO with sp^2 hybridization facilitates interaction with other materials and offers remarkable versatility. By engaging and orienting the chains to one side, the oxygen functional groups on the RGO base plane enhance the crystallinity of PVDF polymer. These properties make RGO highly attractive for energy storage and sensor industries.

Potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$, KNN) is known as a piezoelectric material with a high d_{33}. D. Fast *et al.* have reported a green synthesis method using Lindqvist ion POM, $X_8Nb_6O_{19}$ salt where X represents the Na^+, K^+, or H^+. This new method reduces toxicity concerns while maintaining the material purity compared to previously reported methods.[108] The most important aspect of their research is the production of homogeneous, smooth and dense film which are essential for enhancing the piezoelectric property. Recently, Rambaran *et al.* also reported a novel method for KNN synthesis.[109] They used potassium and sodium nitrates with hexanibate ($[H_xNb_6O_{19}]^{8-x}$) in water. By *ex situ* heating of the precursors they were able to control stoichiometry and phase uniformity of synthesized KNN compare to a solid-state route.[110] They argued that an aqueous route owing to high solubility of polyoxoniobate along with its affinity for coordinating with alkali ions is a developed procedure to produce lead-free piezoelectric KNN. It should be noted that phase uniformity and stoichiometric control are not achievable *via* solid-state process.

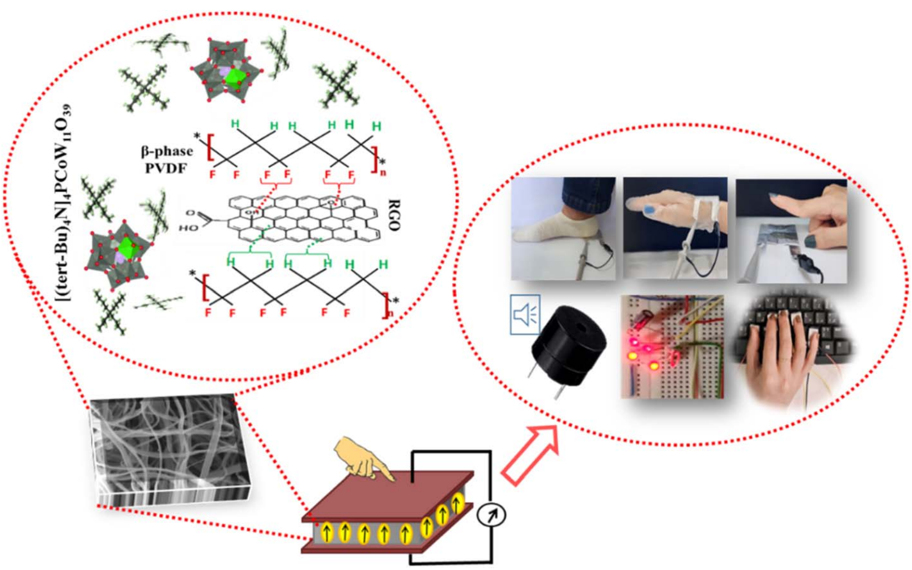

Fig. 11 Using $[(tert\text{-}Bu)_4N]_4PCoW_{11}O_{39}$ as an organic-inorganic hybrid POM to produce nanofibers for PENG fabrication.

POMs exhibit excellent redox properties, however, their inherent solubility leads to poor conductivity. J. E. Madhusree using vanadium-substituted Wells–Dawson POMs to activate biomass-derived carbon for the preparation of nanofabricated electrodes achieving excellent capacitance retention of 94.4% over 4000 cycles and a coulombic efficiency of 82.6%. Also, a piezoelectric buzzer produced an audible sound lasting for 140 seconds.[111]

In another research Keplerate-type POMs were used as friction materials and TiO_2 nanoarrays to fabricate a flexible TENG. They synthesized three form of TiO_2 including nanowires, nanoflowers, and nanosheets, the effect of different Keplerate-type POMs (including $\{Mo_{132}\}$, $\{Mo_{72}Fe_{30}\}$, $\{Mo_{72}V_{30}\}$, and $\{Mo_{72}Cr_{30}\}$) and different morphology of TiO_2 on TENG's performance were investigated. The best electrical output was obtained using $\{Mo_{132}\}$ POM combined with nanoflower TiO_2 array. Fig. 12 shows the assembled TENG by connecting these two layers. The HOMO and LUMO energy levels of POMs and TiO_2 are shown, which indicating that the conduction band of TiO_2 is higher than the LUMO level, thereby enabling electron transfer from TiO_2 level to Keplerate-type POMs. TiO_2 carries a positive charge and POMs are negatively charged. Different Keplerate-types POMs possess varying structure, compositions, and properties so that they showed different energy bands. J. Zhang and colleagues performed Kelvin probe force microscopy (KPFM) tests to explain the performance differences among POMs. The surface potentials of $\{Mo_{132}\}$, $\{Mo_{72}Fe_{30}\}$, $\{Mo_{72}V_{30}\}$, and $\{Mo_{72}Cr_{30}\}$ were measured 1.47, 0.982, 0.964, 0.893 eV respectively. $\{Mo_{132}\}$ showed highest potential and strongest electron capturing ability. It can generate a V_{OC} of 26.2 V, I_{SC} of 125.4 nA, and a transferred charge of 3.6 nC.[112]

W. Du *et al.* fabricated a TENG using Keplerate-type POM *via* spin coating. They proved that modifying surface roughness by changing particle shape and size is an appropriate way to

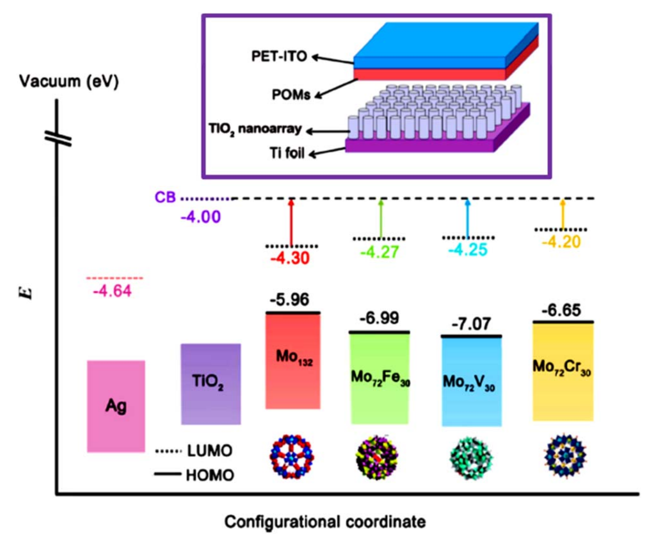

Fig. 12 HOMO and LUMO energy levels of POMs, conduction band of TiO_2, and the work function of Ag for comparison; (inset is the assembled TENG), reproduced from ref. 113 with permission from American Chemical Society, copyright 2025.

overcome weak tribo-property of inorganic tribomaterials. Using these compounds increase heat resistance and improve TENGs stability compare to devices fabricated by organic materials.[113] They used different POMs including $[\{(NH_4)_{42}[Mo_{72}{}^{VI}Mo_{60}{}^{V}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot ca.300H_2O\cdot ca.(CH_3COONH_4)\}\text{-}Mo_{132}]$ and $[\{Na_8K_{14}(VO)_2[\{(Mo^{VI})(Mo_5{}^{VI}O_{21})(H_2O)_3]\}[_{10}\{(Mo^{VI})Mo_5{}^{VI}O_{21}(H_2O)_3(SO_4)\}_2\{V^{IV}O(H_2O)_{20}\}\{V^{IV}O\}_{10}(\{KSO_4\}_5)_2]\cdot 150H_2O)\}\text{-}Mo_{72}V_{30}]$ with blackberry structure. According to their report V_{OC} of 29.3 V, output charge of 8 nC and a power density of 6.25 mW m^{-2} at 300 MΩ were the best results that they obtained.

In another work Y. Su *et al.* using Keggin POMs/g-C_3N_4 composite coated on indium tin oxide/poly(ethylene terephthalate) electrode as friction materials.[115] The maximum V_{OC} was 78 V, current was about 657 nA, and charge of about 15 nC. It seems that this nanocomposite traps electrons and increases charge density of the surface due to the presence of POM.

Polydimethylsiloxane (PDMS) offers advantages of flexibility and transparency and can be used as a base polymer for assembling TENGs as friction material. POM nanoparticles on the surface of PDMS improve its ability to capture the electrons, which increases surface potential and also its surface roughness, thereby enhancing tribo- or piezo-property. Y. Su and co-workers used Dawson-type POMs modified PDMS to fabricate TENGs and introduced these TENGs for wearable self-powered devices. They reported maximum V_{OC} of 30 V and output current of 500 nA.[116]

We recently published another work fabricated PENGs with PVDF and RGO using $H_3PMo_{12-n}V_nO_{40}$, where $n = 0, 2, 3, 4$, to investigate the effect of V^{5+} on the piezoelectric response of the produced PENG.[117] The findings demonstrated that decreasing the vanadium content of HPA improved the piezoelectric characteristics. Additionally, we demonstrated that these HPAs' primary function in enhancing piezoelectric responses is their capacity to store and transmit electrons. Although the presence of HPA increases the active phase of PVDF but the effect is not significant. The resulting composite material was utilized to develop a smart sensor that tracks and detects pressures or strains caused by human activity, offering a quick and practical way to monitor people's motions (Fig. 13).

PVDF/$H_{3-x}Cs_xPW_{12}O_{40}$ composite nanofibers were also synthesized, and the effect of the number of protons in piezoelectric response of these salts was investigated.[118] Without the necessity for a conducting nanofiller, the inclusion of $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ in the composite demonstrated a strong piezoelectric response with a voltage output of 11.12 V under 10 N force, suggesting that this salt could function effectively as a conductive filler. This POM-salt can be utilized as a shallow electron trap to enhance the charge density on the material's surface and increase the electron storage capacity through electron interaction. *Ex situ* synthesis was introduced, and the impact of *in situ* and *ex situ* synthetic methods on the piezoelectric response were also examined. Response's stability and durability of this PENG against an applied force recommends it for energy harvesting applications.

For a deeper understanding of the impact of POMs, the V_{OC}, I_{SC}, charge, and power density data are summarized in Table 1.

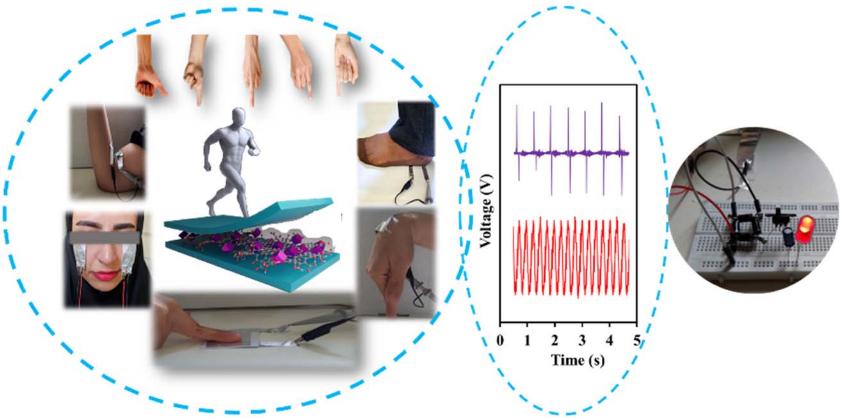

Fig. 13 The V_{OC} of wrist, elbow, finger, heel, facial muscle, fingers forces of PENG fabricated by PVDF, PMo_{12} and RGO.

4. PENGs and TENGs applications

PENGs and TENGs represent two of the most significant advances in the field of self-powered energy harvesting devices, owing to their capability of converting ubiquitous mechanical stimuli from the surrounding environment into usable electrical energy. Their unique ability to enable continuous, maintenance-free operation makes them particularly attractive across a wide spectrum of emerging technologies. In the domain of wearable and flexible electronics, these NGs form the backbone of self-sustaining health monitoring and fitness tracking systems by powering lightweight and compact sensors that eliminate dependence on external batteries.[119] Furthermore, they play a pivotal role in smart fabrics and therapeutic devices, where real-time motion detection and responsive interventions are increasingly demanded for personalized healthcare. Beyond biomedical applications, PENGs and TENGs are also leveraged in intelligent transportation and security infrastructures, where they autonomously energize vehicular safety mechanisms, IoT-based alerts, and distributed sensor networks without requiring extensive power supply frameworks.[120] Environmental surveillance constitutes another rapidly advancing area, as these NGs enable autonomous sensors for continuous monitoring of air quality, ultraviolet radiation, and pollution levels. Their seamless integration with artificial intelligence (AI) algorithms provides enhanced data interpretation, thus contributing to smarter decision-making and predictive analytics. Additionally, the incorporation of hybrid systems, where multiple harvesting modalities are coupled, has significantly improved energy conversion efficiency, establishing PENGs and TENGs as indispensable components in the pursuit of sustainable, off-grid electronic

Table 1 Response comparison of POM-based PENG/TENG devices

Used POM [a]	Voltage (V)	Current	Power density-External resistance	Charge/charge density	NG
$(NH_4)_{42}[Mo_{72}{}^{VI}Mo_{60}{}^{V}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$	29.3	0.75 mA	6.25 mW m^{-2} to 300 MΩ	8 nC	TENG[114]
$[\{Na_8K_{14}(VO)_2[\{(Mo^{VI})(Mo_5{}^{VI}O_{21})(H_2O)_3]\}_{10}$ $\{(Mo^{VI})Mo_5{}^{VI}O_{21}(H_2O)_3(SO_4)\}_2$ $\{V^{IV}O(H_2O)_{20}\}\{V^{IV}O\}_{10}(\{KSO_4\}_5)_2]$	24.5	156 nA	3.75 mW m^{-2} to 300 MΩ	4.2 nC	
$\{Mo_{132}\}$	26.2	125.42 nA	—	3.62 nC	TENG[112]
$\{Mo_{72}Fe_{30}\}$	19.6	120.80 nA	—	3.25 nC	
$\{Mo_{72}V_{30}\}$	16.5	81.75 nA	—	2.92 nC	
$\{Mo_{72}Cr_{30}\}$	9.6	56.88 nA	—	2.21 nC	
PW_{12}	4.0	20 nA	—	1.6 nC	TENG[56]
PMo_{12}	8.2		—		
SiW_{12}	3.5		—		
$SiMo_{12}$	7.2		—		
$K_6P_2W_{18}O_{62}$	5.3		—		
$K_6P_2Mo_{18}O_{62}$	10.5		—		
$(4,4'\text{-}H_2bpy)_2[Zn(4,4'\text{-}bpy)_2(H_2O)_4][ZnW_{12}\text{–}O_{40}]$	395	34.8 µA	1065.8 mW m^{-2} to 50 MΩ	55.1 µC m^{-2}	TENG[50]
$[Cu(H_2TPT)_2(H_2O)_2(ZnW_{12}O_{40})]$	263	22.9 µA	—	32.9 µC m^{-2}	
$[(\textit{tert}\text{-Bu})_4N]_4PCoW_{11}O_{39}]$	6.75	67.8 mA	12 mW cm^{-2} to 10^3 Ω	—	PENG[104]
$PMo_{12}O_{40}$	7.8	20 nA	20.8 µW cm^{-2} to 10^5 Ω	—	PENG[117]
$H_{0.5}Cs_{2.5}PW_{12}O_{40}$	11.2	50.85 µA	570 µW cm^{-2} to 10^3 Ω	—	PENG[118]

[a] Considering the use of different compounds in each case, only the applied POM compound is mentioned. Also, the best reported results are presented. For more information, please refer to the cited reference.

technologies across healthcare, environmental sciences, and advanced wearable systems.[121,122]

Recent progress in self-powered wearable sensor technology emphasizes the integration of advanced functional materials and multimodal energy harvesting mechanisms to ensure autonomous operation entirely independent of external power sources. Such sensors increasingly rely on synergistic harnessing of piezoelectric, triboelectric, thermoelectric, and photovoltaic principles to capture energy from everyday stimuli including mechanical motion, body heat, and ambient light. These capabilities have enhanced their relevance for real-time health monitoring, early disease diagnostics, and human–machine interactive platforms. Their lightweight, breathable, and stretchable architecture renders them suitable for long-term daily usage, while also meeting growing demands for unobtrusive biomedical monitoring. Innovative developments include the application of ionic hydrogels as active materials, valued for their inherent biocompatibility, robust flexibility, ionic conductivity, and self-healing behavior.[123] These properties enable reliable conformation to biological surfaces, elevating their potential as implantable and skin-attachable devices. Nevertheless, challenges persist in areas such as augmenting power density under low-frequency motion, prolonging stability during extended operation, and enhancing overall durability. However, substantial progress is being enabled by interdisciplinary research that bridges theoretical modeling with advanced experimental design, actively driving the transition of these NGs from laboratory prototypes toward practical, real-world implementations.

Hybrid NG systems have recently emerged as a transformative strategy to maximize harvesting efficiency by merging multiple energy conversion principles within a single platform. The complementary effects provided by piezoelectric and triboelectric mechanisms, for example, allow hybrid designs to achieve electrical outputs, stability levels, and conversion efficiencies surpassing what could be attained through any single-mode generator. By integrating these mechanisms within a hybridized framework, it becomes possible to capture a broader range of ambient mechanical stimuli, while simultaneously enhancing power density, frequency response, and current stability. In several advanced designs, additional components such as electromagnetic and thermoelectric generators have been incorporated, further broadening energy harvesting bandwidth and allowing responsiveness to diverse environmental conditions. Such integrated approaches not only minimize energy loss but also expand the applicability of NGs across scenarios demanding reliable and continuous functionality. These hybrid systems therefore represent a significant step toward powering flexible electronic devices, autonomous sensors, and IoT-based architectures in a sustainable and scalable manner.

Due to their structural adaptability and energy harvesting versatility, hybrid NGs are ideally suited for next-generation electronics where lightweight, durable, and maintenance-free solutions are paramount. Their impact spans multiple application sectors: in wearable and biomedical devices, they provide stable and continuous electricity for integrated health assessment and therapeutic feedback systems; in portable and consumer electronics, they capture mechanical energy from user motion or ambient vibrations to prolong device lifespans; in biomedical monitoring, they have the potential to replace batteries in implantable sensors that monitor physiological conditions; and in IoT-enabled smart environments and urban infrastructures, hybrid NGs ensure autonomous operation of distributed sensing networks. Additionally, in environmental monitoring and vibration recovery, they enable sustainable systems capable of scavenging energy from industrial processes or natural activity. Their functionality extends even to human–machine interfaces and artificial skins, where they support highly sensitive, flexible, and durable sensory platforms required for real-time tactile feedback.

Among hybridized approaches, piezoelectric NGs continue to receive considerable research attention for their adaptability across domains beyond conventional wearable electronics. In environmental applications, PENGs are employed for harvesting vibrational energy from sources such as wind, fluid flow, and acoustic activity, effectively powering autonomous distributed sensor arrays without necessitating battery replacements. Their incorporation into large-scale structural health monitoring frameworks, particularly in bridges, tall buildings, and civil infrastructures, exemplifies their transformative impact. Here they provide continuous feedback on mechanical stress, strain, and deformation, offering predictive maintenance capabilities that improve system resilience and public safety. As interdisciplinary collaborations continue to enrich material designs and device engineering, the trajectory of PENGs and TENGs—especially in hybrid platforms—points decisively toward a future where self-powered, autonomous, and intelligent electronics will become integral to healthcare, environmental stewardship, and smart infrastructure systems.[124]

5. Future perspective

Based on my studies in the field of POMs participation in the structure of NGs, it can be concluded that the following methods serve as effective strategies for creating diversity in POMs for synthesizing nanocomposites used in the fabrication of PENGs or TENGs (Fig. 14):

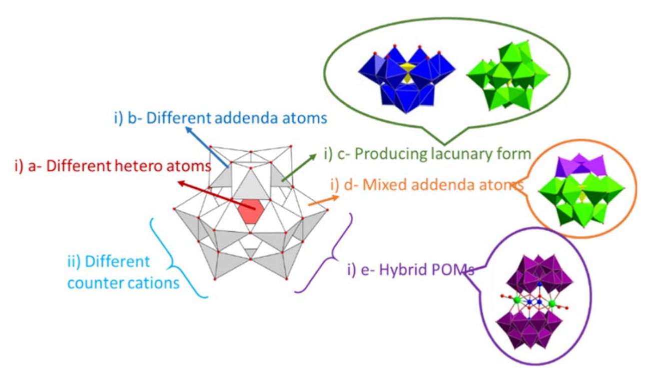

Fig. 14 Different strategies for creating diversity in POMs (i and ii are based on related description in the main text).

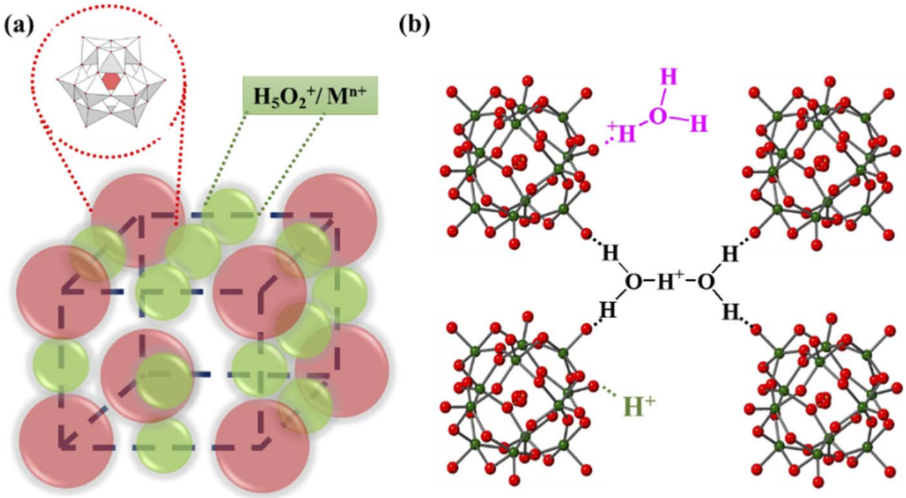

Fig. 15 (a and b) Schematic illustration of the second structure of Keggin type POMs in acidic form or as salt.

(i) Design at atomic/molecular levels: There are several ways to achieve molecular structure diversity: (a) selecting different heteroatoms and/or (b) selecting different addenda atoms; (c) creating lacunary POMs; (d) synthesizing mixed-addenda POMs or POMs substituted with transition metals; and (e) creating hybrid POMs by utilizing organic or organometallic moieties into vacancies or as counter cations of POMs.

(ii) Using acidic form of POMs called HPAs: The secondary structure of HPAs depend on the amount of hydration water[125] which can influence their proton conductivity (Fig. 15). The proton conductivity of these compounds affects their performance in applications such as the fabrication of PENGs or TENGs for energy conversion and storage. Their topology and pore structure can be adjustable by controlling the structural parameters of POMs. This tunability enables the customized design of POMs for a wide range of applications leading to an optimal device performance.

The functional of fillers in composite PVDF especially acidity of the HPAs can significantly enhance its piezoelectric response by influencing several factors as follows:

1. Promotion of β-phase formation: Fillers with acidic surface groups can interact strongly *via* electrostatic force or hydrogen bonding with PVDF chains. During crystallization, this interaction stabilizes the β-phase and aligns the dipoles in PVDF.

2. Increased interfacial polarization: When acidic functional groups are placed in a dielectric matrix such as PVDF produce high interfacial polarization. This effect amplifies the piezoelectric charge coefficient (d_{33}) and contributes to the total dielectric constant by increasing space charge polarization.

3. Improved filler dispersion and interfacial bonding: Functional acidity increases the compatibility between fillers and polymers, which results in stronger interfacial adhesion and improved filler dispersion. Better stress transmission and a more effective conversion of mechanical energy into electrical output are made possible by a well-bonded interface.

4. Induced local electric fields: Acidic sites of fillers can trap charges and create local electric fields, which serve as "nucleation seeds" for β-phase growth and help align PVDF dipoles during processing.

5. Increased dielectric constant: Fillers with acidic surface raise the composite's dielectric constant, which improves energy harvesting efficiency and electromechanical coupling.

To the best of my knowledge, based on published articles, both IPA and HPA have been used as fillers to fabricate NGs. In these POM-materials Mo, W, V, Nb, Fe, Mn, Co, and Cr have used as addenda atoms and in most studies P and Si were used as hetero atoms. As explained above the effect of other addenda and hetero atoms warrant further investigation in the upcoming research.

Moreover, the effect of different structures including Keggin, Wells–Dawson, Anderson–Evans, Lindqvist, and Keplerate types on piezo or tribo responses have been investigated, also a very limited number of lacunary structures have been studied. Therefore, examining other POM structures such as Silverton, especially the greater diversity in the use of lacunary POM-structure containing organic or organometallic moieties is still necessary. Using different salts of POMs and investigation of the effect of various organic cations is regarded as a lack in the current published research that should be addressed.

While significant advancements have been achieved in the field of POM-based NGs, several critical challenges persist. Notably, the limited electrical conductivity of POM materials, issues related to long-term stability under operational conditions, and the relatively high costs of synthesis continue to hinder widespread application. Incorporation of carbon-based fillers and the utilization of such substrates can significantly enhance the electrical conductivity of POMs. Furthermore, the development of POM-based composites, particularly those integrated with conductive polymers or coordination polymers, offers a promising strategy to simultaneously improve both the conductivity and long-term stability of these systems. Also, addressing these barriers requires a concerted effort towards integrating computational and theoretical studies, which offer a powerful means to accelerate the rational design and optimization of POM architectures. Such approaches can elucidate the underlying mechanisms governing material performance and guide the development of more efficient, durable, and cost-effective NGs. Therefore, fostering interdisciplinary research incorporating both experimental and modeling perspectives is essential for realizing the full potential of POM-based energy harvesting systems.

6. Conclusion

Energy has always been the driving force necessary for social developments. However, excessive consumption and the depletion of fossil fuels have made it very challenging to provide sufficient energy for future generations. Therefore, renewable energy and sustainable energy production have became urgent priorities to overcome these issues. In recent decades, scientists have proposed the development of advanced and intelligent technologies for harvesting energy from waste sources such as thermal, vibrational, mechanical or other environmental energies as a solution to these challenges. The use of piezo- and triboelectric properties for the production of NGs to generate electrical energy has garnered significant attention. Extensive research in nanotechnology has led to the application of various inorganic materials to enhance the properties of organic piezo- and triboelectric materials, which not only increases their thermal stability but also improves their piezo- or tribo response. More recently, developments are the using POMs in such productions. There is growing interest in POMs with different structures and piezoelectric polymers with a corresponding growth in the related publications. This paper provides a brief review that discusses and summarizes recent research on incorporating of POMs as widely used and well-known materials in piezoelectric compounds. First, concise background information on piezo- and triboelectric mechanisms and their applications is provided. Next, POMs, their structure, properties, and applications are briefly presented. A detailed review of a range of POM based piezoelectric materials, including ceramics, polymers, and composites follows. POMs can be designed as multifunctional compounds based on different addenda atoms or hetero atoms in their structure, counter cations, second structures, and more. Finally, the future perspective of POM modified NGs across diverse fields are discussed.

Conflicts of interest

The authors confirm that this article content has no conflict of interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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