REVIEW

MATERIALS SCIENCE

Atomically precise metal chalcogenide supertetrahedral clusters: frameworks to molecules, and structure to function

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ABSTRACT
Metal chalcogenide supertetrahedral clusters (MCSCs) are of significance for developing crystalline porous framework materials and atomically precise cluster chemistry. Early research interest focused on the synthetic and structural chemistry of MCSC-based porous semiconductor materials with different cluster sizes/compositions and their applications in adsorption-based separation and optoelectronics. More recently, focus has shifted to the cluster chemistry of MCSCs to establish atomically precise structure–composition–property relationships, which are critical for regulating the properties and expanding the applications of MCSCs. Importantly, MCSCs are similar to II-VI or I-III-VI semiconductor nanocrystals (also called quantum dots, QDs) but avoid their inherent size polydispersity and structural ambiguity. Thus, discrete MCSCs, especially those that are solution processable, could provide models for understanding various issues that cannot be easily clarified using QDs. This review covers three decades of efforts on MCSCs, including advancements in MCSC-based open frameworks (reticular chemistry), the precise structure–property relationships of MCSCs (cluster chemistry), and the functionalization and applications of MCSC-based microcrystals. An outlook on remaining problems to be solved and future trends is also presented.

Keywords: metal chalcogenide, nanocluster, open framework, semiconductor, reticular-chemistry, atomically precise nanochemistry

INTRODUCTION
Nanoclusters, which consist of several or even thousands of atoms, represent an important intermediate state between microscopic atoms and macroscopic matter [1]. A profound comprehension of the composition, structure, and properties of nanoclusters is crucial for exploring or extending their applications. Among the numerous types of nanoclusters, metal chalcogenide supertetrahedral clusters (MCSCs) have attracted great attention since the 1980s for their uniform sizes, well-defined structures, and semiconductor properties [2,3]. Notably, because of their resemblance to II-VI or I-III-VI semiconductor nanocrystals (also known as quantum dots, QDs), MCSCs have been regarded as atomically precise ultrasmall QDs and used to clarify various issues that could not be resolved using traditional QDs, such as the determination of precise site-dependent structure–property relationships. MCSCs can be subdivided into three types: supertetrahedral T\textsubscript{n}-type clusters (T represents the tetrahedra while n indicates the metal layers in each cluster), capped supertetrahedral C\textsubscript{n}-type clusters (The C\textsubscript{n} cluster has a regular T\textsubscript{n} at the core covered with a shell whose stoichiometry is related to the T\textsubscript{n}) and penta-supertetrahedral P\textsubscript{n}-type clusters (The P\textsubscript{n} cluster is regarded as the assembly of four T\textsubscript{n} clusters capped onto the four faces of one anti-T\textsubscript{n} cluster, where an anti-T\textsubscript{n} has the position of cations and anions exchanged when compared with the regular T\textsubscript{n}) [2,3]. This review mainly focuses on “naked” T\textsubscript{n} and P\textsubscript{n} clusters consisting of transition metals(M(I/II)) and group 13/14/16 elements. As C\textsubscript{n} and P\textsubscript{n} clusters with covalently capped ligands have been covered in previous reviews [4,5], only significant advances and some unique cases are presented in this review.

Generally, research on MCSCs can be categorized into three topics: 1) the expansion of the architecture of crystalline MCSC-based frameworks through fabricating clusters with different sizes/compositions and modifying intercluster connecting modes, 2) the discretization of MCSCs in the lattice and their solution processability, and 3) the exploration of the composition–structure–property relationships, functionality, and applications of MCSC-based crystals. Our previous review in 2005 introduce the origin of MCSCs (1989-2005) and the development of topic 1 [2] while the review in 2020 mainly covers the progress of topic 2 and 3 (2005-2020) [3]. Based on these topics, this review provides a systematic overview of the development
of MCSCs over the past three decades, with a focus on four aspects: 1) the development of MCSCs of various types and sizes, 2) the construction of MCSC-based open frameworks, 3) the discretization and dispersibility of MCSCs, and 4) the site-dependent properties and applications of MCSC-based materials.

DEVELOPMENT OF MCSCs: TYPES AND SIZES

The mimicking of natural minerals gave rise to artificial zeolites, and such crystalline porous materials have continued to receive considerable attention since the late 1940s [6]. Initially, porous materials were overwhelmingly dominated by oxide or mixed oxide/fluoride/phosphate matrices. The insulating properties of oxide zeolites and zeolite type materials have seriously restricted the development of photoelectricity applications. Metal chalcogenide zeolite type materials, which integrate semiconductivity and porosity, can overcome these limitations. Unlike the TO₄ (T = Si⁴⁺ or Al³⁺) primary building units of oxide zeolites [7], metal chalcogenide supertetrahedra clusters (MCSC) with tetrahedrally coordinated metal cations and chalcogenide anions serve as the secondary building units in metal chalcogenide frameworks [8]. This section mainly focuses on MCSCs by treating them as virtual isolated clusters, whereas MCSC-based open frameworks are discussed in the next section.

The first series of MCSCs is supertetrahedral Tn-type clusters with the molecular formula MₓEₙ (where x = [n(n + 1)(n + 2)]/6; y = [(n + 1)(n + 2)(n + 3)]/6). Tn clusters have a structure corresponding to the regular tetrahedral shaped fragments of the sphalerite (cubic ZnS) phase, which is characterized by orderly distributed multivalent metal components with high tunability (Fig. 1) [2,3]. The evolution of Tn clusters and related microcrystals has relied on modifying local charge balance, mostly by selecting the valence of the constituent metals. For example, a T2 cluster consisting of bicoordinate anionic sulfur (μ₄-S²⁻) usually contains M⁺⁺ ions (e.g., Ge⁺⁺ or Sn⁺⁺) [9]. By contrast, M³⁺ ions (e.g., In⁺³ or Ga⁺³) can ensure the existence of tricoordinate anionic sulfur (μ₃-S³⁻) to give rise to a T3 cluster [10]. However, in a T4 cluster, which is usually stabilized by M⁴⁺ ions (e.g., Zn⁺⁺, Cd⁺⁺, Mn⁺³, Fe⁺³, Co⁺³, or Ni⁺³), the tetrahedral coordination of anionic sulfur (μ₄-S⁴⁻) can occur within the core [11]. As the cluster size increases to T5, one low-valent M⁺ ion (e.g., Cu⁺) located at the cluster center is connected to four μ₄-S⁴⁻, and the 12 metal sites adjacent to the four μ₄-S⁴⁻ are shared by high/low-valent M³⁺/M⁺ ions (e.g., In⁺³/Cu⁺) [12]. Furthermore, with an increasing number of μ₄-S⁴⁻, a distinct core−subshell−shell structure emerges in the largest T6-ZnInS cluster (i.e., ZnS@ZnInS@InS) [13]. Larger Tn clusters (n ≥ 7) are also predicted to adopt such a core−subshell−shell structure but with an increased core area, expanding toward the cubic ZnS phase. Essentially, this behavior follows Pauling’s electrostatic valence rule, where the valence of an anionic sulfur should be the same as or nearly equal to the sum of its electrostatic bonds with adjacent cationic metals. Such a systematic arrangement of cationic metals endows Tn clusters with multivalent metal components that are highly tunable, which is critical for investigating precise structure−composition−property relationships and tuning properties. Notably, high valent metal cations, such as M³⁺/M⁺, are not indispensable in the construction of Tn-type clusters. It has been demonstrated that low-valent metal cations, such as Co⁺² [14], Cd⁺² [15], and Zn⁺² [16], are capable of constructing T2 or T3 clusters when the surplus negative charge of anionic sulfur can be well compensated by suitable covalently-protected ligands. In addition, monovalent Ag⁺ cations, which were used to build silver chalcogenide tetrahedral clusters [17,18], can also construct T3 clusters [19,20] although it was considered to be challenging due to the argentophilic interactions [21].

In addition, as another excellent illustration of Pauling’s electrostatic valence rule in the construction of MCSCs, the oxychalcogenide o-Tn cluster, which is regarded as a set of pseudo-Tn clusters, can be formed by inserting anionic oxygen (O²⁻) into the adamantane cages of the Tn cluster and increasing the valence of the cationic metals (i.e., o-T2-SnOS [22], o-T3-SnOS [23], and o-T4-InSnOS [24]) to ensure local charge balance.
(Fig. 1). Notably, the largest o-T5 cluster dominated by In\(^{3+}\) has a unique InO\(_8\) core with one non-tetrahedrally-coordinated In\(^{3+}\) connected to four tetrahedrally coordinated interstitial oxygens (O\(_i\)) and four triangularly coordinated substitutional oxygens (O\(_s\)) [25]. Interestingly, another MCSC containing non-tetrahedrally coordinated In\(^{3+}\) ions is the unique TO2 cluster, which has a NaCl-type [In\(_{n_0}S_{3}\)] core bearing octahedrally coordinated In\(^{3+}\) coupled with four [In\(_{n_2}S_{4}\)] hexagonal rings and four T2-[In\(_{n_0}S_{3}\)] clusters [26] (Fig. 1). Instead of inserting anions, the absence of core metal ions is also an effective strategy to achieve new pseudo-T\(_n\) clusters. These coreless clusters with a central void have a single metal tetrahedral site vacant in the regular T\(_n\) lattice, such as T5-InS (coreless) [27] and T5-CdInS (coreless) clusters [28,29]. Evidently, in both of these clusters, to compensate for the local charge mismatch, the valence of the metal coordinated to \(\mu_-S^2\) is increased as compared to that of the metal in the T5-CuInS cluster [12]. As another type of pseudo-T\(_n\) cluster, super-supertetrahedral T\(_p,q\) clusters, such as T2,2-InSnS (pseudo-T4) [30], T4,2-MnInS (pseudo-T8) [31], and T3,2-InSnS (pseudo-T6) [32], are constructed by the hierarchical fusion of four T\(_n\) clusters.

Unlike “naked” polyanionic T\(_n\) type clusters, capped supertetrahedral Cn-type clusters with covalently protected ligands on the surface (e.g., –SR or –SeR) are usually electrically neutral or have a low negative charge [2,4,5]. Regardless of the capping ligands, Cn-type clusters have the molecular formula M\(_x\)E\(_{n+y}\) (where \(x = [n(n+1)(n+2)]/6 + [4(n+1)(n+2)]/2 + 4; y = [(n+1)(n+2)(n+3)]/6 + [4(n+2)(n+3)]/2 + 4\). Structurally, the Cn cluster has a core possessing a regular fragment of the cubic ZnS phase covered with four corner barrelanoid cages consisting of the hexagonal \(\alpha\)-ZnS phase (Fig. 1) [2,4,5]. In addition, each barrelanoid cage can be independently rotated by 60\(^\circ\) (around the three-fold axis of the tetrahedron), resulting in four additional variants denoted as Cn,\(_m\) clusters, where \(m\) refers to the number of corners that have been rotated relative to the original Cn cluster [33]. For example, the so-far largest Cn cluster is the C3,4 cluster with the composition of Cd\(_{23}X_{33}(SPh)_{66}(H_2O)_4\) (X = S, Se) [34]. Generally, the structural deformation caused by corner rotation does not affect the properties significantly; therefore, the performance is usually considered to depend on the \(n\) value, and Cd-17 (C1), Cd-32 (C2), and Cd-54 (C3) were usually used to emphasize the size of the cluster. When compared with the multivalent metal constituents in Tn clusters, the employment of ER\(^+\) instead of E\(^{2+}\) makes charge balance less complicated and also less diverse, especially local charge balance. Therefore, Cn clusters are usually composed of M\(^{2+}\) (e.g., Cd\(^{2+}\), Mn\(^{2+}\), or Hg\(^{2+}\)) [4,5,35-38]. Owing to this elimination of interference from multiple components, Cn clusters are usually referred to as ultrasmall QDs for the systematic study of size-dependent optical and electronic properties.

Another series of MCSCs consists of penta-supertetrahedral Pn-type clusters, which can be structurally considered as assemblies of four T\(_n\) clusters capped on the face of one anti-T\(_n\) cluster, where the anti-T\(_n\) cluster has the same geometrical features as the T\(_n\) cluster but with the positions of the cations and anions exchanged (Fig. 1) [2,4,5], whose configuration is very similar to the supertetrahedral zintl cluster [39]. Until now, only two types of Pn clusters have been observed, namely, P1 and P2 clusters, each of which can be further classified by the presence or absence of covalently capped ligands. Capped P1 clusters usually have the formula [M\(_{n_0}EPh\(_m\)]\(^{1+}\) (M = Zn or Cd; E = S, Se, or Te) [40,41]. By contrast, “naked” P1 clusters have the formula [M\(_{n_0}E(SPh)_m\)]\(^{10+}\) (M = Mn, Fe, Co, or Zn; E = S or Se) [42-45]. Synthetically, P2 clusters have been obtained with or without capping ligands; for example, three P2 clusters were found in 3D frameworks (P2-Li\(_{n_0}In\(_{2n_0}\)S\(_{8n_0}\) (ICF-26) [46], P2-CuInSnS (MCOF-1 and MCOF-2) [47], and P2-CuGaSnS (MCOF-4) [48]) and two discrete examples of capped P2 (P2-Cu\(_{n_0}In\(_{n_0}\)Se\(_{n_0}\)(SePh)_4(PPh)_4) [49] and P2-Cu(M)SnS (M = Ga, In, or both) [50] were synthesized.
MCSCs IN OPEN FRAMEWORKS: RETICULAR CHEMISTRY

Crystalline MCSC-based porous framework materials have attracted great attention owing to the effective integration of porosity with semiconductor properties [2]. From the perspective of synthetic chemistry, the choice of sulfur provides the following advantages: 1) anionic sulfur has a larger ionic radius than oxide and fluoride ions, which favors tetrahedral coordination for cationic metals, thus allowing the formation of Tn clusters and leading to the preparation of chalcogenide zeolites type frameworks; 2) theoretically, the higher polarizability of anionic sulfur may make M–S–M angles more flexible than the T–O–T angles in oxides, resulting in more flexible frameworks that can better accommodate a template; and 3) the arrangement of the tetrahedra in MCSCs is the same as that in bulk matter [8]. The initial synthetic methodologies for metal chalcogenide frameworks were analogous to those for oxide zeolites, with O\(^+\) replaced by S\(^-\) and oxyphilic metals (e.g., Si\(^4+\) or Al\(^3+\)) replaced by sulfophilic metals (e.g., Ge\(^4+\)/Sn\(^4+\) or Ga\(^3+\)/In\(^3+\)). However, the synthetic methods for metal chalcogenide frameworks have evolved over the past three decades, and current approaches can be classified as follows: 1) room- or lower-temperature solution methods (e.g., diffusion, evaporation, or recrystallization), 2) high-temperature solid-state methods, and 3) hydro(solvo)thermal or ionothermal methods. Generally, polyanionic MCSCs assemble into multilevel structures (1D chains, 2D layers, or 3D frameworks) through corner sharing modes, with alkali metal ions, protonated organic amines, or ionic liquids serving as structure-directing agents in addition to providing charge compensation [2,5].

Research on MCSC-based open frameworks has received attention since the work by Bedard et al. in 1989 [51]. Early advances in the construction of such frameworks involved the assembly of transition metal cations (e.g., Mn\(^2+\), Cu\(^2+\), or Ag\(^+\)) with T2-Ge\(_{3n}\) clusters based on the efforts of the Yaghi, Ozin, and Parise groups [52-54]. The first breakthrough in MCSC framework chemistry can be regarded as the formation of a framework with larger cluster size. In 1998, Parise and co-workers obtained the first T3-InS-based 3D open framework with a diamond topology, which suggested that structural variants were not limited to the Ge-S system but also possible in the In-S system [10]. Two identical subnetworks were found to exhibit undesired interpenetration. Subsequently, Yaghi and co-workers isolated three noninterpenetrated T3-InS based frameworks, including ASU-31 with sodalite network (Fig. 2a), ASU-32 with a tetragonal CrB\(_4\) network (Fig. 2b) [55], and ASU-34 with a single diamond network [56]. Considering low-valent transition metals as a synthetic parameter provided a series of new open frameworks built from larger Tn clusters, such as the first T4-CdInS-based 3D diamond-type framework CdInS-44 (Fig. 2c) [11], the first T5-CulnS-based 3D diamond-type framework UCR-17 [12], and T5-CdInS-based 2D layers [28]. Recently, the first T6-ZnInS-based 2D layered networks were also obtained [13]. Interestingly, as the cluster size increased, in addition to the common intercluster connection mode (μ\(_4\)-S\(^2-\)) (Fig. 3a), the other connection modes of S\(^-\) were also developed. For example, the μ\(_4\)-S\(^2-\) connection mode was first observed in T4-based UCR-8 (Fig. 3b) [57], affording a cubic C\(_3\)N\(_4\) net with the μ\(_3\)-S\(^2-\) and T\(_4\) clusters as nodes (Fig. 2d). The μ\(_4\)-S\(^2-\) connection mode was first observed in T5-CulnS-based CIS-11 [58] and then in T4-ZnInS-based ITF-9 (Fig. 3c) [59]. Seemingly, the structural diversity of Tn-based frameworks is dominated by the type of Tn cluster (i.e., size and composition) and the intercluster connection modes (i.e., μ\(_4\)-S\(^2-\), μ\(_3\)-S\(^2-\), and μ\(_1\)-S\(^2-\)). Structure-directing agents with different charges, sizes, and shapes also play an extremely important role in the framework formation, as the M–E–M bond angles can be effectively modified by the cations serving as structure-directing agents through Coulomb forces or H-bonding (H-E), leading to chalcogenide frameworks with various topologies, such as Dabco-MnGS-SB1 (ABW) [60], UCR-1 (lvt) [61], CSZ-5 (bor) [62], CMF-1 (qtz), CMF-3 (mog) [63], T\(_2\)-(o-T\(_3\)) (PtS) [64], SOF-27 (NAB) [65], and SOF-20 (gsi) [66] (Fig. 2e-l).
The continuous enrichment of MCSC-based frameworks and a good comprehension of synthesis methods allowed the focus to be shifted from the expansion of framework types to porosity applications. In this regard, the primary issue became effectively removing the organic templates while maintaining framework stability. Unfortunately, most of the frameworks collapsed during the ion exchange process. However, Feng and co-workers achieved a breakthrough by constructing a family of chalcogenide zeolite analogs (UCR-20–23) with excellent thermal and chemical stabilities and available void space [30]. These zeolite analogs were built from T2 clusters consisting of M\(^{3+}/M^{4+}\) (e.g., Ge\(^{4+}/Ga^{3+}\) or Sn\(^{4+}/In^{3+}\)) by adopting the classic stability rule of zeolite synthesis, whereby a higher M\(^{4+}/M^{3+}\) ratio provides a more stable structure. Replacing M\(^{3+}\) with M\(^{2+}\) (Zn\(^{2+}\) or Cd\(^{2+}\)) gave another family of high-silica-zeolite-like chalcogenides (CPM-120–123) with an M\(^{4+}/M^{2+}\) ratio close to 3. Notably, CPM-120-ZnGeS exhibited reversible adsorption with high capacity and affinity for CO\(_2\), and could act as a robust photocatalyst [67].

Most MCSC-based frameworks have been built from clusters with the same order, which follows Pauling’s fifth rule, the rule of parsimony, which states that “the number of essentially different kinds of constituent in a crystal tends to be small”. Nevertheless, hybrid frameworks built with different sizes or types of MCSCs are highly desirable to enrich the available structures and simultaneously realize the coexistence of multiple metal components in a single framework. In this regard, by unifying two charge-complementary synthetic strategies via the combination of M\(^{3+}/M^{4+}\), M\(^{3+}\), and M\(^{4+}\) ions, a series of hybrid MCSC-based frameworks has been successfully constructed, including T2 (GaSnS)-(o-T3) (SnOS) [64], OCF-42 (ZnGaGe(Sn)Se) built on T2-T4 clusters [68], CIS-52 built on T2 (InGeS)-T5 (CuInS) [69], UCR-19 built on T3 (GaS)-T4 (ZnGaS) [70], UCR-15 built on T3 (InS)-T5 (coreless) (InS) [27], IOS-35 built on T3(InS)-(o-T5) (InOS) [71], and OCF-45 built on T4 (MnInS)-T5 (coreless) (MnInS) [72]. In addition, efforts in the In-S (Se) or Cd-S domain have also revealed the possibility of constructing MCSC-based frameworks using hybrid P1 and T2 clusters [73,74] or hybrid P1 and C1 clusters [63]. Furthermore, by doping the In-S system with Sn\(^{4+}\) atoms to obtain clusters with appropriate global charges, a new kind of hybrid assembly between T3 and T3,2 clusters has been obtained [32].

However, following decades of development, the traditional sulfur-bridging modes have resulted in a “bottleneck” in the construction of new structures. Inspired by metal–organic frameworks, the introduction of organic ligand bridges has been considered an effective approach to diversify the intercluster connection modes. Moreover, the resulting organic–inorganic hybrid framework materials may favor functional synergy. In fact, as early as 2005, bipyridine and its derivatives were introduced into C\(_n\)-based superstructures (COV-\(q\)) [33,75]. By contrast, transition metal ions in C\(_n\) clusters have a stronger coordination ability to organic ligands than the trivalent or tetravalent metals distributed at the corners of T\(_n\) clusters. In addition, trivalent or tetravalent metals in T\(_n\) clusters preferentially coordinate sulfur over organic ligands, especially in a reaction environment with large amounts of anionic sulfur. The third advance was realized by Vaqueiro et al., who assembled T\(_n\) clusters with 1,2-di(4-pyridyl)ethylene (Fig. 3d) [76], affording T3-GaS-based 1D and 2D covalent organic–inorganic structures. However, bipyridine ligands seem to be unwilling to form 3D framework structures with MCSCs due to their nonrigid configuration, which may make the resultant 3D framework thermodynamically unstable. Inspired by the construction of zeolitic imidazolate frameworks (ZIFs), Feng and co-workers subsequently successfully introduced imidazolate and its derivatives as linkers to form a series of 3D supertetrahedral cluster imidazolate frameworks (SCIFs), wherein the larger T4-CdInS (compared with the T3-GaS in bipyridine system) was found in SCIF-8 and SCIF-9 (Fig. 3e) [77]. In addition to N-donor ligands, carboxylate (trimesic acid), which has been widely used in the construction of metal organic frameworks (MOFs), has also been introduced as a linker into the MCSC-based structures, affording T3-InS-based 1D chain, T4-FeInS-based 0D trimer superlattice, and o-T5-InOS-based 2D honeycombed
layer (Fig. 3f) [25].

As mentioned above, transition metal ions, such as Mn$^{2+}$, Ag$^+$, and Cu$^+$, have been used to facilitate the assembly of MCSCs by the Yaghi, Ozin, and Parise groups [52-54], but this approach is limited to small T2 clusters. In principle, the addition of a low-valent transition metal (M$^{+}/2^+$) to the reaction system induces the formation of larger clusters, with the transition metal present in the cluster core to stabilize the multicoordination of anionic sulfur instead of outside the cluster in a linkage. However, this issue can be addressed by adding high-valent M$^{4+}$ (i.e., Ge$^{4+}$ or Sn$^{4+}$) to the reaction at a suitable ratio. The high-valent metals are selectively distributed at the cluster vertexes, which effectively lowers the negative charge of the terminated anionic sulfur and correspondingly reduces the possibility of further bonding of such sites to M$^{3+}$ or M$^{4+}$ while retaining their ability to coordinate low-valent M$^+$. Based on this strategy, single Cu$^+$ ion bridged MCOF-3 (Fig. 3g) and MCOF-4 (MCOF = metal chalcogenide open framework) composed of larger T4-CuGaSnS and P2-CuGaSnS clusters have been obtained [48]. Such copper-rich MCOF materials have been applied as nonenzymatic glucose-sensing catalysts and exhibit promising sensing performance. In addition to copper ions, trivalent antimony (Sb$^{3+}$) ions have also been applied to the assembly of MCSCs, in the form of either a single Sb$^{3+}$ ion or a small Sb$_x$S$_y$ cluster. For example, the single Sb$^{3+}$ cation can be incorporated into the T2-InS based framework as the tri-coordinated bridge mode [78]. Sb$_5$S$_{10}$ and Sb$_6$S$_{12}$ can respectively serve as the tetra-coordinated linkers, giving rise to two T4-MnInS based frameworks MCOF-6 (Fig. 3h) and MOCF-7 [79]. Interestingly, due to the steric hindrance or torsion stress of those two linkers, the resultant two frameworks exhibited different symmetry of space group (I$4_1/a$ for MCOF-6 and C$2/c$ for MOCF-7), further leading to the different local coordination environment of [Mn$_4$S] core in T4-MnInS clusters. More recently, two new T3 based supraclusters were obtained by incorporating Sb$^{3+}$ ions as the linker, which further make up a 2D 4,4-grid layered MCOF-31 (Fig. 3i) and a 3D pcu topological framework MCOF-32, respectively [80].

**MCSCs IN DISCRETE SUPERLATTICES: NANOCHEMISTRY**

Compared with MCSCs that are confined in extended frameworks, the isolated form in a superlattice provides a valuable opportunity to study the physical and chemical properties of MCSCs as genuine nanomaterials. In particular, solution-processable MCSCs are similar to II-VI or I-III-VI colloidal QDs, which can provide advantageous models for investigating various issues that are difficult to be clarified using QDs. For example, a homologous series of C$_n$(CdSe) clusters with well-defined electronic structures favors the systematic study of size-dependent optical and electronic properties [81], and the obtained insights may contribute to the understanding of CdSe QDs. The highly tunable multimetal components of Tn clusters make it possible to study the photo-/electrochemical properties induced by metal components and precise doping sites and establish precise structure–composition–property relationships. Compared with the covalently capped C$_n$ clusters that are usually isolated in a discrete superlattice with good solution dispersity, “naked” Tn clusters, especially large ones, preferentially assemble into extended frameworks to decrease the overall negative charge of individual clusters. In principle, to obtain discrete MCSCs, the bridging ability of the anionic sulfurs at corners should be regulated to isolate the tetrahedra and the high negative charge of individual clusters should be reduced and balanced to promote successful crystallization from the mother liquor. To address these issues, a combination of “multivalent metal complementarity” (or M$^{4+}$ termination strategy) and “superbase-assisted crystallization” has been proposed [3], which affords a set of discrete T4-MGaSnS clusters (M = Cu$^+$, Mn$^{2+}$, or Zn$^{2+}$) (OCF-40) [82], a discrete T5-CuGaSnS cluster (ISC-21-CuGaSnS) [83], and three isostructural discrete P2-CuMSnS cluster (M = Ga$^{3+}$, In$^{3+}$, or both) [50]. To visualize the “multivalent metal complementarity” strategy, an abstract representation of an isolated T4 (OCF-40) cluster is shown in Fig. 4. As mentioned previously, the metal sites with different valences are
selectively distributed in the supertetrahedron to satisfy the local charge balance [84], where $\mu_4^{-}\text{S}^2$ at the core is connected to low-valent $M^{+/2+}$ ions (region 1), $\mu_3^{-}\text{S}^2$ at the face is connected to $M^{+/2+}$ and $M^{3+}$ ions, and $\mu_2^{-}\text{S}^2$ at the edge is connected to $M^{3+}$ or $M^{4+}$ and $M^{4+}$ ions (region 2), and terminal $S^{-}$ are connected to $M^{3+}$ and/or $M^{4+}$ ions (region 3). Notably, high-valent $M^{4+}$ ions (usually Sn$^{4+}$), which are typically used for preparing small T2 or T3 clusters, are introduced. The preferential distribution of these ions at the corner sites controls the bridging ability of the corner $S^2-$, usually resulting in the discretization of clusters. In addition, the incorporation of a large amount of $M^{4+}$ inevitably decreases the negative charge of the individual clusters, thus favoring crystallization and subsequent dispersion. For the "superbase-assisted crystallization" strategy, superbase molecules, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and piperidines (PRs), which are more prone to protonation, create highly concentrated cations in the mother liquor, thus stabilizing the negatively charged MCSCs. Moreover, the approximately in-plane molecular configuration of the superbases is conducive to the crystallization of MCSCs. Compared with the control in the bridging ability of the corner $S^2-$, capping four corners of MCSCs with terminated organic ligands is the most straightforward and effective method to isolate them. Although this method is very common in Cn and Pn system while it is really challenging in Tn system. The first success is the discrete hybrid T3-GaS (NC$_7$H$_9$)$_4$, in which the corner $S^2-$ were replaced by covalently bonded 3,5-dimethylpyridine [85]. Instead of replacing the corner $S^2-$, a discrete T3-ZnGaSnSe was obtained with four corners covalently terminated by [Mn(TEPA)]$^{2+}$ (TEPA=tetraethylenepentamine) metal complexes [86]. In addition, DBN molecule has been experimentally demonstrated as an effective terminal agent, being similar with the 3,5-dimethylpyridine, whose N atom not only has the ability to protonate but also has the ability to coordinate with cationic metals, affording a family of isolated hybrid supertetrahedral chalcogenide clusters (denoted as ISC-n) [87] and a unique T3-InS based dimer with six corners terminated by DBN [88,89]. More recently, imidazolium-based ionic liquids were found to be effective in preparing discrete MCSCs, and the resulting discrete superlattice exhibited good dispersibility [90].

Although an effective method has been found to address the issue of discretization, the solution dispersibility of larger Tn clusters with a high negative charge remains challenging because of the strong electrostatic interactions caused by the close stacking of MCSCs and organic cations. In this regard, several groups have presented feasible solutions. For example, Dai and co-workers used a high ionic strength medium (Li$^+\text{-DMF}$) to overcome the strong ionic forces in the crystal and realized solution-processable T5-CuInS clusters [91]. The morphology and stability of the dispersed T5-CuInS clusters were characterized by high-resolution transmission electron microscopy and electrospray ionization mass spectrometry. Our group used the principle of similar dissolution to achieve the dispersion of discrete T4 clusters (OCF-40) in piperidine and obtained multimetallic sulfide nanoparticles (MMSNPs) composed of 6–8 T4 clusters [92]. Similarly, the dispersion of P2-CuMSnS (M = Ga$^{3+}$, In$^{3+}$, or both) clusters was realized using a 1:1 mixture of H$_2$O and acetone [50]. In addition, Li and co-workers replaced S in T4-CdInS with Se to weaken the energy of the H-bonds between T4 clusters and organic cations, thus achieving solubility in dimethyl sulfoxide (DMSO) [93]. Furthermore, the packing modes have recently been found to have an important effect on dispersibility with T4-MlnS (M = Zn$^{2+}$ or Fe$^{3+}$) clusters having a sodalite-net loose-packing pattern in a discrete lattice exhibiting excellent water dispersibility [94].
PROPERTIES AND APPLICATIONS

To highlight the uniqueness and significance of these cluster-based semiconductor materials, in this section, the properties and applications of MCSC-based crystals are discussed hierarchically based on two aspects: 1) atomically precise site-dependent properties, including photo-/electrochemical properties induced by internal dopant/defect sites and external S/Se-related interfacial properties; and 2) the performance of MCSC-based crystalline semiconductor materials and functional composites.

Atomically Precise Site-Dependent Properties

Doping is an effective method for tuning the electric structures of semiconductors and their physical or chemical properties. While nanocrystals often exhibit inherent structural ambiguity and random doping sites, the atomically precise metal sites in T\textsubscript{n} clusters and their selective distribution provide an opportunity to gain insights into their precise structure–component–property relationships. The discrete T\textsubscript{5}-CdInS (coreless) cluster, with a single vacant metal site inside, can be doped with monometal ions. For example, the vacancy can be doped with a monocopper ion through a postmodification strategy to afford new T\textsubscript{5}-CuCdInS clusters with enhanced visible-light-responsive photoelectric properties as compared to those of the parent T\textsubscript{5}-CdInS (coreless) cluster (Fig. 5a) [29]. Similarly, monomanganese doping inserted the characteristic Mn\textsuperscript{2+} energy levels into the T\textsubscript{5}-CdInS host, thus allowing charge or exciton energy transfer from the host lattice to the Mn-related orbitals upon excitation. This process resulted in an unusual red emission (630 nm) from the d–d spin-forbidden \( ^{4}T_{1} \rightarrow ^{6}A_{1} \) transition in Mn\textsuperscript{2+} originating from the local “crystal lattice strain” caused by the mismatch of M–S bond lengths in the “Mn@CdS@InS core–shell” structure. Notably, the photoluminescence (PL) intensity is proportional to the Mn\textsuperscript{2+} doping level in the microcrystals composed of T\textsubscript{5}-CdInS (coreless) clusters (Fig. 5b) [95]. Furthermore, such single vacant sites can function as nanosegregation sites that eliminate possible interference between two types of dopants, giving rise to single-crystal white emission via the codoping of Cu\textsuperscript{+} and Mn\textsuperscript{2+} at an appropriate ratio (Fig. 5c) [96]. In addition to PL, vacancy point and antisite defects in T\textsubscript{5}-CdInS (coreless) clusters have been revealed to induce electrochemiluminescence (ECL), which can be tuned by the doped Mn\textsuperscript{2+} ions. As displayed in Fig. 5d, the ECL emission of the internal vacancy centered at 585 nm is suppressed when monomanganese is doped into the vacant site of T\textsubscript{5}-CdInS (coreless), which gives rise to ECL emission centered at 615 nm [97]. However, such postmodification doping strategies can lead to the following problems: 1) slow ion diffusion dynamics inevitably affect the doping level, that is, not all T\textsubscript{5}-CdInS (coreless) clusters are doped with Mn\textsuperscript{2+} ions; and 2) corrosion by organic solvents during the doping process may damage the host cluster and create a large number of defect points, thus providing additional nonradiative pathways. These problems are responsible for the low PL quantum yield (0.53%) [95] and low ECL efficiency (0.0085%) [97] of the postmodification Mn-doped T\textsubscript{5}-CdInS clusters. Fortunately, these problems can be addressed using the \textit{in situ} Mn\textsuperscript{2+} doping method, which provides controllable Mn\textsuperscript{2+} doping levels and simultaneously reduces the defect points, affording a high PL quantum yield (43.68%), which is 82-fold higher than that of the sample prepared by postmodification doping [98], as well as a high ECL efficiency (27.1%) [99].

It is well known that the photophysical behavior of doped semiconductors depends not only on the concentration and location of the dopants but also on the surrounding coordination environment, such as the bond length, spatial symmetry, and interactions with ambient dopants [100]. Extensive research has been conducted on the former factor using colloidal QDs, whereas the latter factor can be studied using T\textsubscript{n} clusters. For example, doping a single Mn\textsuperscript{2+} ion into T\textsubscript{4}-ZnInS and T\textsubscript{6}-ZnInS yields two MnZnS@InS core–shell structures with ZnS cores of different thicknesses, in which the Mn\textsuperscript{2+} ions most likely replace the Zn\textsuperscript{2+} site on the face of the tetrahedra owing to similarities in bond length. Temperature-dependent PL spectra
revealed that $T_4$-$MnZnInS$ displays a larger red shift ($\sim 27$ nm) ($\text{Fig. 6a}$) than $T_6$-$MnZnInS$ ($\sim 15$ nm) ($\text{Fig. 6b}$), which is ascribed to the “buffering effect” of the ZnS core, that is, a larger ZnS core can weaken the torsion or distortion of Mn–S bonds and the coordination geometry of the Mn dopant that arises from the compressive strain from the outer “In-S” shell [13]. A similar phenomenon was also observed in lightly doped $T_4$-$MnCdInS$ ($MnCdS@InS$) and heavily doped $T_4$-$MnInS$ ($MnS@InS$), as the temperature-sensitive PL of the lightly doped cluster was ascribed to the larger local “crystal lattice strain” caused by the nonsymmetric $MnCdS$ core [101]. By contrast, in the heavily doped $T_4$-$MnInS$ with a $Mn_S$ core, Mn–Mn magnetic coupling was expected to affect the PL behavior. Thus, the PL behavior of two $T_4$-$MnInS$ with different symmetrical cores ($D_{2d}$ or $C_1$) and Mn–Mn distances was investigated, revealing new insights into the dominant role of symmetry-directed Mn–Mn dipole–dipole interactions over distance-directed spin-exchange interactions in modulating the PL quenching mechanism ($\text{Fig. 6c and d}$) [79]. More recently, ultrafast transient spectroscopy has been employed to investigate the excited state dynamics of the internal metal sites. For example, an intercluster charger transfer process was revealed in a hybrid $T_3$-$T_4$ framework ($\text{UCR-19}$), in which the photogenerated charge carriers were directionally transferred from the $T_3$-$InS$ clusters to the $T_4$-$Mn(Fe)InS$ clusters owing to the staggered band gap alignment between the molecular heterojunctions, followed by radiative/nonradiative recombination at the $Mn^{2+}/Fe^{2+}$ centers [102]. In addition, an intracluster charge transfer process was revealed in the $P_2$-$CuMInS$ ($M = Ga, In$, or both) cluster, in which three decay components in the femtosecond transient absorption spectra with systematic amplitude changes were attributed to the different constituent $M^{3+}$ ions. Finally, a core–shell (anti-$T_2(CuSnS)$ to $T_2(Ga/InSnS)$) charge transfer dynamics was revealed [50].

The regulation and doping of internal metal sites not only influence the photo-/electrochemical properties but also the photo-/electrocatalytic performance. For instance, a series of hybrid hydrogen evolution reaction electrocatalysts was prepared by loading MMSNPs composed of $T_4$-$MGaSnS$ ($OCF-40$) clusters on N-doped reduced graphene oxide. The Mn/Co/Zn-codoped catalyst exhibited the best electrocatalytic activity with the lowest overpotential of $176$ mV at $10$ mA cm$^{-2}$ and a small Tafel slope of $43$ mV dec$^{-1}$. This result was subsequently investigated using density functional theory (DFT) calculations, which revealed that the $\Delta G_{\text{ads}}$ of H atoms and the energy barriers for the dissociation of H atoms from $H_2O$ could be tuned by the doped metals, while the Mn/Co/Zn-codoped $T_4$ cluster had a near-zero adsorption free energy for H atoms and a low dissociation barrier for $H_2O$ to produce adsorbed H atoms [103]. Similarly, a series of hybrid photocatalysts was prepared by coating MMSNPs on the surface of silver nanowires (Ag-NWs), in which an ultrathin Ag$_2$S interface layer formed to act as an adhesive between the MMSNPs and the Ag-NWs. This system exhibited tunable visible-light photocatalytic performance owing to the synergistic effect of the multimetallic constituents of the MMSNPs [92]. In addition to the transition metals, the interrupted $In^{3+}$ sites in the $T_2$-$InSeO$ cluster of the CSZ-5-InSe framework were demonstrated to be electrocatalytically active centers for the oxygen reduction reaction (ORR); the electro-/photoelectrochemical performance was easily manipulated by replacing $In^{3+}$ at interrupted sites with $Bi^{3+}$, and the cyclic voltammograms (CVs) for the ORR on CSZ-5-InSe/CB and CSZ-5-InBiSe/CB show that $Bi^{3+}$ doping at interrupted sites can deteriorate the catalytic activity [62] (Fig. 6e).

In addition to the metal component, the chalcogen elements can also be modified to effectively tune the electronic structure of MCSC-based crystals and their properties. For example, as mentioned above, the replacement of $S^2-$ with $Se^2-$ can promote the dispersibility of $T_4$ clusters. Moreover, subsequent photocatalytic experiments showed that the $H_2$ evolution rate increases significantly as the Se content in the $T_4$ cluster increases [93]. Another interesting case is the nonlinear variation in the composition and optical band gap of CSZ-5-InSe as the $Se^2-$ sites are gradually replaced with $S^2-$, which is due to the structural
features of this open framework [104]. In addition, the nonlinear control mechanism of CSZ-5 could result
in an optimal balance between resistivity, band gap, and carrier mobility, thus affording an excellent X-ray
detector with a high figure of merit for the mobility–lifetime product \((7.12 \times 10^{-4} \text{ cm}^2 \text{V}^{-1})\) [105] (Fig. 6f).

Owing to the soft Lewis base nature of chalcogen elements (S, Se, and Te), the polarizability of the
internal surface of MCSC-based frameworks is much larger than that of oxide zeolites and porous carbons
[106]. In addition, the highly negative charge density of MCSC-based frameworks can afford a high cation
uptake capacity, with the multidimensional intersecting channels allowing rapid ion diffusion and offering a
unique kinetic advantage. These features are highly desirable for ion exchange and gas adsorption. For
example, UCR-20 exhibited a highly selective and rapid uptake of radionuclide Cs\(^+\) after activation through a
stepwise ion-exchange strategy [107], and the activated UCR-20 also showed highly selective adsorption of
CO\(_2\) over N\(_2\) [108]. Moreover, an investigation of the Cs\(^+\) exchange kinetics in T\(_4\)-InSnOS-based framework
materials by Zhang and co-workers found that the small pore pockets created by the two interpenetrating
frameworks act as pincers to selectively capture Cs\(^+\) ions [109]. In addition, a series of purely inorganic
MCSC-based frameworks, which was prepared \textit{in situ} using alkali cation templates, exhibited high ionic
conductivities (up to \(1.8 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}\)) at room temperature and moderate to high humidity because of their
high anionic framework polarizability and high concentrations of mobile alkali metal cations [110].

Cluster and/or Framework-Dependent Functional Properties

In addition to the abovementioned site-dependent properties, MCSCs can also exhibit cluster and/or
framework-dependent properties. Thus, this section focuses on the properties and applications of
MCSC-based crystalline semiconductor materials and MCSC-based functional composites. Generally,
MCSC-based framework materials have been investigated as photocatalysts for hydrogen generation from
water [67,111], dye degradation [112], and the reduction of CO\(_2\) into CH\(_4\) [113]. Furthermore, electrocatalysis
applications, mainly focusing on the ORR [62,114,115], continue to be reported. In addition to these
conventional applications, some unique properties inherent to MCSCs have also been explored. For example,
the intrinsic advantages of the integrated porosity and semiconductor properties make MCSC-based
frameworks a good model for investigating host–guest chemistry. For instance, by encapsulating acridine
orange (AO) in the nanopores and loading rhodamine B (RhB) on the surface of the semiconductor porous
framework UCR-20, respectively, a multistep vectorial host-guest energy transfer can be clearly observed, in
which the ultraviolet energy harvested by the host framework can transfer to the first-order acceptor AO
molecules, then onto the second-order acceptor RhB molecules, resulting in visible light emission [116].
Similarly, a series of host–guest synergetic electrocatalysts was fabricated by embedding Cu\(_2\)S [117] or
S-doped Ni(OH)\(_2\) [118] nanoparticles in the nanopores of UCR-20. Generally, the host framework not only
plays an important role in improving the electrocatalytic performance of the composite but also acts as a
sulfur source and stabilizer. Owing to their good aqueous dispersibility, as mentioned above, discrete T\(_2\)
clusters have been used as precursors to construct crystalline porous frameworks. These clusters can also be
used as precursors to prepare amorphous porous semiconductor materials, such as chalcogenide aerogels,
and Kanatzidis and co-workers have made a great contribution in this area [119]. Typically, T\(_2\) clusters (GeS,
GeSe, or SnSe) are proportionally mixed with K\(_2\)[PtCl\(_4\)] in aqueous solution, resulting in all the Cl ligands
being replaced with the terminal S or Se atoms of T\(_2\) clusters, which eventually affords gelation [120]. The
noncentrosymmetry of the tetrahedral T\(_n\) clusters is a prerequisite for the generation of nonlinear optical
(NLO) materials, especially for second harmonic generation (SHG). For example, using acentric \([\text{ABa}_2\text{Cl}]\)
polycations (A = Rb or Cs) to replace Rb\(^+\) cations in parent centrosymmetric RbGaS\(_2\), two new
noncentrosymmetric salt-inclusion chalcogenides \([\text{ABa}_2\text{Cl}][\text{Ga}_4\text{S}_{10}]\) with the ordered arrangement of
NLO-active T\(_2\)-Ga\(_4\)S\(_{10}\) clusters were achieved, which demonstrated strong phase-matchable SHG intensities,
high laser-induced damage thresholds, and a wide transparency window [121] (Fig. 7).

CONCLUSION AND OUTLOOK

In conclusion, the development of MCSC chemistry over the past three decades has centered on the expansion of MCSCs (size, type, and composition) and MCSC-based frameworks, and the exploration of their properties and applications. Essentially, the development of MCSCs is inseparable from the development of MCSC-based frameworks and vice versa. Although it is undeniable that more elaborate structures can still be achieved through the assembly of MCSCs using traditional sulfur connection modes, new synthesis strategies are also essential. To date, only a few types of organic ligands have been successfully introduced into MCSC-based frameworks. Therefore, from the perspective of developing new structures and realizing organic–inorganic synergy materials, the exploration of organic–inorganic hybrid frameworks should be extended. In regard to the discretization and dispersibility of MCSCs, various effective strategies have been presented and promising results have been achieved. However, the dispersion of clusters in solution, especially monodispersion, remains a significant challenge that must be addressed for postmodification and subsequent applications. In addition to the materials covered in this review, MCSCs have also been demonstrated to form surfactant-encapsulated complexes (SECs) with quaternary ammonium salts bearing long carbon chains. These SECs are promising precursors for the amorphous self-assembly of MCSCs. In addition, MCSCs are promising triplet sensitizers for photon upconversion or reactive oxygen species generation, for which MCSC composition and site-dependent regulatory mechanisms are likely to be significant.

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Figure 1. Development of the metal chalcogenide supertetrahedral cluster (MCSC) family, including basic supertetrahedral \( T_n \)-type clusters, capped supertetrahedral \( C_n \)-type clusters, penta-supertetrahedral \( P_n \)-type clusters, pseudo-\( T_n \) clusters (oxychalcogenide o-\( T_n \) clusters, super-supertetrahedral \( T_{p,q} \) clusters, and coreless \( T_n \) clusters), and TO2 clusters. Note that the MCSCs illustrated here are the firstly reported cases corresponding to years when they were reported. \( T_2 \) [9], \( T_3 \) [10], \( T_4 \) [11], \( T_5 \) (coreless) [27], \( T_5 \) [12], \( T_6 \) [13], o-\( T_2 \) [22], o-\( T_3 \) [23], o-\( T_4 \) [24], o-\( T_5 \) [25], \( T_2,2 \) [30], \( T_4,2 \) [31], \( T_3,2 \) [32], \( C_1 \) [35], \( C_2 \) [36], \( C_3 \) [34], covalently protected \( P_1 \) [40], naked \( P_1 \) [42], covalently protected \( P_2 \) [49], naked \( P_2 \) [46], TO2 [26].
Figure 2. MCSC-based open frameworks with various topological structures. (a) ASU-31 with a sod net, where T3 clusters are treated as nodes [55]; (b) ASU-32 with a CrB3 net, where T3 clusters are treated as nodes [55]; (c) CdInS-44 with a dia net, where T4 clusters are treated as nodes [57]; (d) UCR-8 with a cubic-C3N4 net, where μ3-S2- and T4 clusters are treated as nodes [57]; (e) Dabco-MnGS-SB1 with an ABW net, where single Mn2+ ions and T2 clusters are treated as nodes [60]; (f) UCR-1 with an lv3 net, where T4 clusters are treated as nodes [61]; (g) CSZ-5 with a bor net, where T2-InSe and interrupted T2-InSeO are treated as nodes [62]; (h) CMF-1 with a quartz (qtz) net, where P1 clusters are treated as nodes [63]; (i) CMF-3 with a mog net, where P1 and C1 clusters are treated as nodes [63]; (j) T2-(o-T3) with a PtS net, where T2 and o-T3 clusters are treated as nodes [64]; (k) SOF-27 with a NAB net, where T3 clusters are treated as nodes [65]; and (l) SOF-20 with a gsi net, where T2 are treated as nodes [66].
Figure 3. Typical sulfur connection modes in MCSC-based frameworks, exemplified by (a) $\mu_2$-$S^2$ in CdInS-44 [11], (b) $\mu_3$-$S^2$ in UCR-8 [57], and (c) $\mu_4$-$S^2$ in ITF-9 [59]. Hybrid MCSC-based frameworks: (d–f) assembly of clusters and inorganic ligands [76,77,25]. (g) single linearly-coordinated Cu$^+$ ion linker in T4-CuGaSnS based MCOF-3 [48], (h) Sb$_3$S$_6$ linker in T4-MnInS based MCOF-6 [79], and Sb$^{3+}$ ions in T3-based suprcluster of MCOF-31 [80].
Figure 4. Site-selective distribution in a large Tn supertetrahedron, where $\mu_4$-$S^2$ at the core is usually connected to low-valent $M^{1+}$ ions (region 1); $\mu_3$-$S^2$ at the face is connected to $M^{1+}$ and $M^{3+}$ ions, and $\mu_2$-$S^2$ at the edge is connected to $M^{3+}$ or $M^{3+}$ and $M^{4+}$ ions (region 2); and terminal $S^2$- are connected to $M^{3+}$ and/or $M^{4+}$ ions (region 3). Adapted with permission from [84].
Figure 5. (a) Photoelectric response of T5-CdInS (coreless) and Cu-doped T5-CdInS. (b) PL of undoped and Mn-doped T5-CdInS with different doping levels (the inset shows the illuminated crystals). (c) Single-crystal white emission of Cu/Mn-codoped T5-CdInS (the inset shows the illuminated crystal). (d) ECL of T5-CdInS (coreless) and Mn-doped T5-CdInS. Adapted with permission from [29,95-97].
Figure 6. Temperature-dependent PL spectra of (a) Mn-doped T4-ZnInS and (b) Mn-doped T6-ZnInS. (c) Photoluminescence excitation (PLE) and PL spectra of MCOF-6, and (d) PL spectrum of MCOF-7. (e) CVs of ORR on CSZ-5-InSe/CB and CSZ-5-InBiSe/CB, and (f) the resistivity and mobility-lifetime product of S-doped CSZ-5-InSe versus the S doping ratio. Adapted with permission from [13,79,62,105].
Figure 7. Polycation-substitution-induced centrosymmetric transformation of T2-based materials and particle-size-dependent SHG intensities of T2-based crystals with incident lasers at 1910 and 1064 nm. Adapted with permission from [121].