Toward high-quality colloidal metal halide perovskite nanocrystals

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Colloidal metal halide perovskite nanocrystals (NCs) exhibit tremendous applications in light-emitting diodes (LEDs), photovoltaics, laser diodes (LDs), memristors and radiation sensors, owing to their outstanding optoelectronic properties, facile synthesis process and low cost. However, they have been facing formidable challenges in optoelectronic devices due to their poor reliability. Typically, perovskite NCs are coordinated with ammonium cations (R-NH_3^+) and carboxyl anions (R-COO^-), which form ionic pairs that tend to quickly desorb, eventually leading to perovskite decomposition (Figure 1A).[1] Environmental factors, such as water, oxygen, light and heat, exacerbate this process. Ligand shedding not only affects the chemical structural stability of NCs but also sharply degrades their performance. Although deep trap states (i.e., interstitial and anti-site defects) in the electronic structure are almost absent due to the energetically difficult dislocation of ions in the perovskite lattice, A- and X-site vacancies on the surface of NCs lead to shallow energy levels, which increase nonradiative recombination rates (Figure 1B).[2] In particular, the photoluminescence quantum yields (PLQYs) of the NCs are only 10-20% in the UV/blue region. Thus, strengthening the interactions between ligands and the surface of NCs is one of the keys to enhancing the stability and optoelectronic properties simultaneously.

To address this issue, the surfaces of perovskite NCs have been stabilized and passivated using organic ligands either through *in-situ* synthesis or post-synthesis modifications.[3] The former approach passivates surface defects by adding excess oleic acid and oleamine, while the latter approach has been greatly exploited using different ligands or halide salts, which are expected to

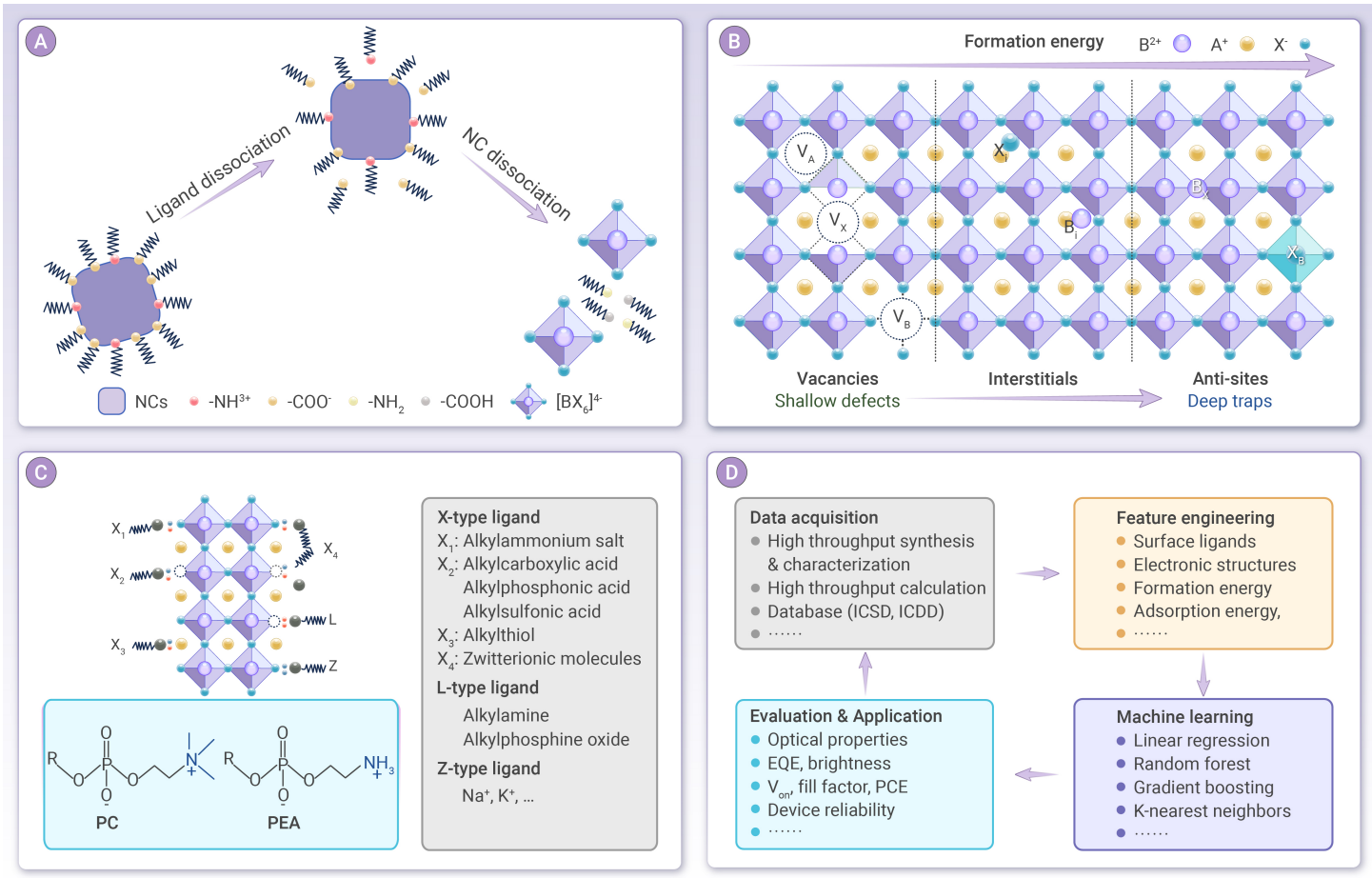

Figure 1. Schematic diagram of the ligand chemistry of metal halide perovskite NCs (A) Decomposition diagram of the perovskite NCs due to the desorption of weakly bound ligands. (B) Typical defects in perovskite NCs, including vacancies, interstitials, and anti-sites with increasing formation energy. (C) Summary of the three types of ligands employed to passivate the surface of perovskite NCs and the molecular structures of zwitterionic PC and PEA. The black dots represent the electrons donated by the perovskite NCs, while the red dots represent the electrons donated by the surface ligands. (D) The workflow of machine learning-assisted discovery of high-quality perovskite NCs for photoelectric devices.

fill the A- and X-site vacancies. As shown in Figure 1C, these ligands are divided into X-, L-, and Z-types according to their covalent bond classification. X-type ligands are one-electron donors that donate one electron to metal cations or halide anions; L-type ligands can be considered as two-electron donors that share a lone pair of electrons with B^{2+} ions acting as Lewis bases; and Z-type ligands are two-electron acceptors that receive a lone pair of electrons from halide anions acting as Lewis acids. Although some ligand modifications are expected to result in stable perovskite

surfaces, excessively strong interactions between the ligands and perovskite NCs readily outcompete the relatively low internal lattice energy, which leads to ionic metathesis reactions with the NC core. Zwitterionic molecules (X_4-type) have two functional groups with positive and negative charges that simultaneously bind to the A- and X-sites. Therefore, their surface binding energy can be optimized by balancing interactions between two head groups and the NCs to obtain high-quality perovskite NCs. However, how to rationally design these zwitterionic ligands is still unclear.

Recently, Kovalenko et al. proposed a molecular engineering strategy involving zwitterionic phospholipid ligands for the construction of high-quality metal halide perovskite NCs with simultaneous excellent optical properties and colloidal stability.[4] The affinity between zwitterionic alkyl phosphocholine (PC) ligands and green lead halide perovskite (e.g., $FAPbBr_3$) NCs was primarily governed by the structure of the zwitterionic headgroup, especially by the geometric fitness of the anionic and cationic moieties into the surface lattice sites, which was confirmed by combining molecular dynamics simulations with Fourier transform infrared (FTIR) and solid-state nuclear magnetic resonance (NMR) spectroscopy. Although the PC ligands stabilized the surface of the $FAPbBr_3$ NCs, the surface coverage with the PC ligands did not exceed 50%. To tailor the affinity, phosphoethanolamine (PEA) with head groups of the primary ammonium moiety was employed as the surface ligand, which results in a better geometry with A-sites and allows for a surface coverage of up to 100%. Correspondingly, the hexadecyl-PEA-capped $FAPbBr_3$ NCs demonstrated much better colloidal stability than the hexadecyl-PC-capped NCs. In addition, the colloidal stability is also strongly associated with the structure of the ligand tail (R). Thus, a library of PEA-based capping ligands with different tail groups, including aliphatic, aromatic, halogenated or polyether structures, was constructed and investigated systematically. As a result, the green perovskite NCs capped with PEA-R (R is poly(ethylene)glycol and poly(propylene)glycol tails) exhibit long-term colloidal stability, monodispersity, and excellent optical properties. The PEA-capped $FAPbBr_3$ NC films exhibit a PLQY as high as 96-97%, and the single NCs exhibit nearly non-blinking (94% "ON" state), which is highly important for future ultrahigh-definition display applications.

However, these metal halide perovskite NCs still face many challenges: (i) unsatisfactory PL properties in the UV/blue region; (ii) unsatisfactory overall stability against light, heat, water, oxygen and electric fields; (iii) unclear structure-activity relationships; and (iv) different material characteristics (i.e., energy level structure, light absorption efficiency, conductivity, and carrier mobility) for multi-optoelectronic device applications. Thus, in addition to the surface ligands, the optical properties and stability of perovskite NCs are also closely related to their chemical structure, composition, crystal formation energy and electronic structure. How to design and synthesize perovskite NCs quickly and rationally for high-performance optoelectronic devices is the focus and hot spot of future research in this field. The conventional trial and error method for developing high-quality perovskite NCs is slow. In contrast, machine learning has been considered a promising tool for accelerating the discovery of high-quality colloidal perovskite NCs. The workflow (Figure 1D) of these methods can be summarized as follows: data acquisition, feature engineering, machine learning, evaluation, and application. Despite some successes,[5] many challenges remain to be addressed, such as the establishment of a database, feature selection, validity of the used machine learning models, and understanding of the physicochemical mechanisms, which therefore requires more scientists in theoretical physics, computational science, and experimentation to explore it.

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DECLARATION OF INTERESTS

The authors declare no competing interests.