

## FEATURE ARTICLE



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## Green-route manufacturing towards future industrialization of metal halide perovskite nanocrystals

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Perovskite nanocrystals (PeNCs) with excellent optical properties have attracted tremendous research interests and have been considered as promising candidates for new-generation optoelectronic devices. Over the past few years, numerous efforts have been made to overcome the challenges in terms of sustainable manufacturing of PeNCs and related devices and systems, including the solvents used in precursor preparation, antisolvents and perovskite materials for the fabrication of devices and systems, and remarkable progress has been made. However, the usage of toxic, organic solvents in the synthesis of PeNCs poses a threat to the ecosystem and human health, which has hindered the progress in the commercialization and industrialization of PeNCs. This has promoted the development of green solvents for the sustainable manufacturing of PeNCs. In this Feature Article, a state-of-the-art green method for the synthesis of PeNCs is presented, in which the solvents of low toxicities are underlined in contrast to the reported Reviews which focus on toxic solvents for the preparation of precursor solutions. We then focus on green, aqueous methods for the preparation of PeNCs, including conventional perovskite and double PeNCs, by summarizing our previous research efforts and studies. In particular, pure water as the greenest solvent is introduced for the preparation of PeNCs, and the parameters affecting the size and optical characteristics of PeNCs, such as sonication time and ligands for post-treatment, are discussed. The strategies of using a passivation layer to improve the aqueous stability of PeNCs are reviewed, which are grouped into organic polymers and inorganic semiconductors. We highlight the challenges and possible solutions in the green manufacturing and applications of PeNCs. The green routes discussed in this article for the synthesis of PeNCs are expected to be a major step forward for the commercialization and industrialization of the fabrication of PeNCs. It is anticipated that green manufacturing will continue to be the mainstream in the synthesis and fabrication of PeNCs.

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### 1. Introduction (background, significance, and development)

Environmental conservation has always been a global topic for sustainable development. Green manufacturing is one of the effective approaches to solve this front-burner issue from the perspective of industrial manufacturing. The fabrication of materials is a core component in industrial manufacturing, especially for semiconducting materials. Green chemistry plays an indispensable and significant role in the advancement of this field. For green manufacturing and chemistry, green metrics need to be considered to evaluate new methodologies for the study of products. Some green metrics have been

adopted by a variety of organisations, such as the biomedical industry. The Process Mass Intensity (PMI)<sup>1</sup> is currently the most favourable metric, in which solvents, reactants, reagents, elements, *etc.* are incorporated.<sup>2</sup> On top of that, less hazardous chemical syntheses have been reported as one of the green chemistry principles.<sup>3</sup> Therefore, solvents used in the synthesis of materials are a critical key to the establishment of green chemistry and green manufacturing.

Semiconductor nanocrystals (NCs), also called quantum dots when they exhibit a quantum confinement effect, are one of the functional semiconducting materials used in optoelectronics. Traditional semiconductor NCs, especially group II–VI (*e.g.*, CdS, CdSe, CdTe and ZnSe), group IV–VI (*e.g.*, PbS, PbSe), group III–V (*e.g.*, InP), *etc.*, have been well developed with excellent optoelectronic properties. However, there are concerns about the hazardous effects of these traditional semiconductor NCs on the environment and human health, which pose a threat to their further industrialization. For group II–VI

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NCs, a high-cost complex process is needed for the fabrication of core-shell structures to enhance the stability.<sup>4,5</sup> The toxic Cd element (heavy metal) hinders their further development to some extent for commercial applications. For group IV–VI NCs, poor optical stability, low efficiency, and limited spectrum range (infrared) impede their development.<sup>6–8</sup> Although heavy metal-free III–V group NCs have achieved high photoluminescence quantum yields (PLQYs) of >90%,<sup>9,10</sup> they still require epitaxial shells to improve the stability, which makes the synthesis of heavy metal-free III–V group NCs a high-cost and complicated process.

Perovskite NCs (PeNCs) with a range of merits, such as high light absorption coefficient, high defect tolerance, high colour purity, high brightness, and facile fabrication, have exhibited promising applications in LEDs (light-emitting diodes).<sup>11–13</sup> With the unique property of the multiple exciton generation (MEG) effect,<sup>14</sup> PeNCs have been extensively investigated in solar cells.<sup>15–17</sup> Up to now, the external quantum efficiency (EQE) of PeNC LEDs for red, green, and blue emissions have reached ~29%,<sup>18</sup> ~22%,<sup>19</sup> and ~12%,<sup>20</sup> respectively, and the EQE of PeNC-based solar cells has been up to 17.4%.<sup>21</sup> These achievements have stimulated fascinating research of PeNCs over the past decade.

The most frequently used methods for the synthesis of PeNCs include hot injection (HI)<sup>22</sup> and antisolvent methods<sup>23,24</sup> (also called the ligand-assisted reprecipitation (LARP) technique). However, the toxic, organic solvents used in the preparation and/or synthesis processes for these methods hinder the large-scale manufacturing and industrialization of PeNCs. Green-route synthesis of PeNCs is called for solving this crucial and urgent issue from the view of sustainable development, which, however, has not been reported in Review and Feature articles. There is an urgent need to provide a comprehensive overview of the progress in green manufacturing, which is based on aqueous solution methods, towards future industrialization to be made in the field. In this Feature article, the current green approaches (including the use of green solvents) for the preparation of PeNCs are summarized. In particular, aqueous solution methods are focused as a mainstream and promising approach for the green synthesis of PeNCs. The prospects for promising green methods as a critical part of the fabrication of optoelectronic devices are presented.

## 2. Environmental, health, and safety analyses of green solvents

Solvents are indispensable materials for the preparation of precursor solutions for the continuous manufacturing of PeNCs *via* solution-based methods, especially the antisolvent method. Compared to the HI method, the antisolvent method is cost-effective, simple, and energy-saving, and has been considered as a more promising approach for the fabrication of PeNCs. Driven by the technological evolution in the synthesis of PeNCs, the PeNC-based devices and systems have achieved remarkable advancement and been in the initial stage of com-

mercialization. In this case, industries will evaluate whether the solvents used in the manufacturing are green or not, and require that the solvents have negligible or reduced toxicity to be environment-friendly for the eco-system, health and safe to human beings.<sup>25–27</sup> The European Chemical Agency has been managing chemicals through REAR (Registration, Evaluation, Authorization, and Restriction) legislation for the protection of human health and the environment.<sup>28</sup> Environmental, health, and safety (EHS) criteria have been established and adopted for the identification of green solvents.<sup>29</sup> Industries and pharmaceutical companies have scored solvents, using EHS assessments, and categorized and ranked solvents through the EHS scores. In 2016, Prat *et al.* reported a modified methodology to meet the CHEM-21 (short for Innovative Medicines Initiative (IMI)-CHEM21 public private partnership) criteria for solvents.<sup>29</sup>

Table 1 lists the ranking of “classical” solvents guided by CHEM21. The score of EHS is highlighted in red (7–10), yellow (4–6), and green (1–3), which is perspicuous for users to identify the solvents. The higher the score, the more hazardous the solvent. With no exception, the most used solvents for the preparation of precursor solutions and for further synthesis of perovskite materials are included in this list of chemicals, such as *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and so forth. As can be seen from Table 1, DMF has a score of 9 for health, and 3 and 5 for safety and environment, respectively. This indicates that DMF is a toxic chemical to the human body and has been classified as a highly hazardous solvent. For DMSO, the EHS number is 5, 1, and 1. The toxicity is more mitigatory than DMF.

Also, globally harmonized system (GHS) of Classification and Labelling of Chemicals defines DMF as a severely harmful solvent while DMSO is not. These data point to that DMSO can be considered as a green solvent for the fabrication of perovskites, compared to DMF. However, DMSO has a higher boiling point of 189 °C than DMF of 153 °C (according to the OSHA (Occupational Safety and Health Administration) safety data sheets), which makes DMSO an energy-consuming solvent in the preparation of materials and devices. Therefore, the mixture of DMF and DMSO is commonly used as the solvent to prepare precursor solutions, based on their common properties of aprotic dipolar,<sup>30–34</sup> which are capable of dissolving lead-containing halide salts (such as PbI<sub>2</sub>, PbBr<sub>2</sub>, *etc.*). Another role of DMSO is to slow down the crystallization rate of crystals in precursor solutions to produce crystals and films of high-quality since a small crystallization rate allows monomers in precursor solutions to reach equilibrium sites on crystals.<sup>35</sup> Gamma-butyrolactone (GBL, which is not shown in Table 1) is another most-used aprotic dipolar solvent. According to the GHS data, GBL is not a severely harmful solvent. In contrast to DMF and DMSO, GBL has a greater solvent polarity that enables stronger miscibility for salts (powder precursors), which can enhance the density of films and the crystallinity of bulk crystals. Nevertheless, GBL possesses a low viscosity of 1.7 mPa s and a high boiling point of 204 °C, which results in a time-consuming evaporation process.

Table 1 CHEM21 guided "classical" solvents. Reprinted with permission from ref. 29 Copyright (2016) the Royal Society of Chemistry

| Family        | Solvent                | BP (°C) | FP (°C) | Worst H3xx <sup>a</sup> | H4xx | Safety score | Health score | Env. score | Ranking by default | Ranking after discussion <sup>b</sup> |
|---------------|------------------------|---------|---------|-------------------------|------|--------------|--------------|------------|--------------------|---------------------------------------|
| Water         | Water                  | 100     | na      | None                    | None | 1            | 1            | 1          | Recommended        | Recommended                           |
| Alcohols      | MeOH                   | 65      | 11      | H301                    | None | 4            | 7            | 5          | Problematic        | Recommended                           |
|               | EtOH                   | 78      | 13      | H319                    | None | 4            | 3            | 3          | Recommended        | Recommended                           |
|               | i-PrOH                 | 82      | 12      | H319                    | None | 4            | 3            | 3          | Recommended        | Recommended                           |
|               | n-BuOH                 | 118     | 29      | H318                    | None | 3            | 4            | 3          | Recommended        | Recommended                           |
|               | t-BuOH <sup>c</sup>    | 82      | 11      | H319                    | None | 4            | 3            | 3          | Recommended        | Recommended                           |
|               | Benzyl alcohol         | 206     | 101     | H302                    | None | 1            | 2            | 7          | Problematic        | Problematic                           |
| Ketones       | Ethylene glycol        | 198     | 116     | H302                    | None | 1            | 2            | 5          | Recommended        | Recommended                           |
|               | Acetone                | 56      | -18     | H319                    | None | 5            | 3            | 5          | Problematic        | Recommended                           |
|               | MEK                    | 80      | -6      | H319                    | None | 5            | 3            | 3          | Recommended        | Recommended                           |
|               | MIBK                   | 117     | 13      | H319                    | None | 4            | 2            | 3          | Recommended        | Recommended                           |
|               | Cyclohexanone          | 156     | 43      | H332                    | None | 3            | 2            | 5          | Recommended        | Problematic                           |
| Esters        | Methyl acetate         | 57      | -10     | H302                    | None | 5            | 3            | 5          | Problematic        | Problematic                           |
|               | Ethyl acetate          | 77      | -4      | H319                    | None | 5            | 3            | 3          | Recommended        | Recommended                           |
|               | i-PrOAc                | 89      | 2       | H319                    | None | 4            | 2            | 3          | Recommended        | Recommended                           |
|               | n-BuOAc                | 126     | 22      | H336                    | None | 4            | 2            | 3          | Recommended        | Recommended                           |
| Ethers        | Diethyl ether          | 34      | -45     | H302                    | None | 10           | 3            | 7          | Hazardous          | HH                                    |
|               | Diisopropyl ether      | 69      | -28     | H336                    | None | 9            | 3            | 5          | Hazardous          | Hazardous                             |
|               | MTBE                   | 55      | -28     | H315                    | None | 8            | 3            | 5          | Hazardous          | Hazardous                             |
|               | THF                    | 66      | -14     | H351                    | None | 6            | 7            | 5          | Problematic        | Problematic                           |
|               | Me-THF                 | 80      | -11     | H318                    | None | 6            | 5            | 3          | Problematic        | Problematic                           |
|               | 1,4-Dioxane            | 101     | 12      | H351                    | None | 7            | 6            | 3          | Problematic        | Hazardous                             |
|               | Anisole                | 154     | 52      | None                    | None | 4            | 1            | 5          | Problematic        | Recommended                           |
|               | DME                    | 85      | -6      | H360                    | None | 7            | 10           | 3          | Hazardous          | Hazardous                             |
| Hydrocarbons  | Pentane                | 36      | -40     | H304                    | H411 | 8            | 3            | 7          | Hazardous          | Hazardous                             |
|               | Hexane                 | 69      | -22     | H361                    | H411 | 8            | 7            | 7          | Hazardous          | Hazardous                             |
|               | Heptane                | 98      | -4      | H304                    | H410 | 6            | 2            | 7          | Problematic        | Problematic                           |
|               | Cyclohexane            | 81      | -17     | H304                    | H410 | 6            | 3            | 7          | Problematic        | Problematic                           |
|               | Me-cyclohexane         | 101     | -4      | H304                    | H411 | 6            | 2            | 7          | Problematic        | Problematic                           |
|               | Benzene                | 80      | -11     | H350                    | None | 6            | 10           | 3          | Hazardous          | HH                                    |
|               | Toluene                | 111     | 4       | H351                    | None | 5            | 6            | 3          | Problematic        | Problematic                           |
|               | Xylenes                | 140     | 27      | H312                    | None | 4            | 2            | 5          | Problematic        | Problematic                           |
| Halogenated   | DCM                    | 40      | na      | H351                    | None | 1            | 7            | 7          | Hazardous          | Hazardous                             |
|               | Chloroform             | 61      | na      | H351                    | None | 2            | 7            | 5          | Problematic        | HH                                    |
|               | CCl <sub>4</sub>       | 77      | na      | H351                    | H420 | 2            | 7            | 10         | Hazardous          | HH                                    |
|               | DCE                    | 84      | 13      | H350                    | None | 4            | 10           | 3          | Hazardous          | HH                                    |
| Aprotic polar | Chlorobenzene          | 132     | 29      | H332                    | H411 | 3            | 2            | 7          | Problematic        | Problematic                           |
|               | Acetonitrile           | 82      | 2       | H319                    | None | 4            | 3            | 3          | Recommended        | Problematic                           |
|               | DMF                    | 153     | 58      | H360                    | None | 3            | 9            | 5          | Hazardous          | Hazardous                             |
|               | DMAc                   | 166     | 70      | H360                    | None | 1            | 9            | 5          | Hazardous          | Hazardous                             |
|               | NMP                    | 202     | 96      | H360                    | None | 1            | 9            | 7          | Hazardous          | Hazardous                             |
|               | DMPU                   | 246     | 121     | H361                    | None | 1            | 6            | 7          | Problematic        | Problematic                           |
|               | DMSO <sup>c</sup>      | 189     | 95      | None                    | None | 1            | 1            | 5          | Recommended        | Problematic                           |
|               | Sulfolane <sup>c</sup> | 287     | 177     | H360                    | None | 1            | 9            | 7          | Hazardous          | Hazardous                             |
| Miscellaneous | HMPA                   | >200    | 144     | H350                    | None | 1            | 9            | 7          | Hazardous          | HH                                    |
|               | Nitromethane           | 101     | 35      | H302                    | None | 10           | 2            | 3          | Hazardous          | HH                                    |
|               | Methoxy-ethanol        | 125     | 42      | H360                    | None | 3            | 9            | 3          | Hazardous          | Hazardous                             |
|               | Carbon disulfide       | 46      | -30     | H361                    | H412 | 9            | 7            | 7          | Hazardous          | HH                                    |
| Acids         | Formic acid            | 101     | 49      | H314                    | None | 3            | 7            | 3          | Problematic        | Problematic                           |
|               | Acetic acid            | 118     | 39      | H314                    | None | 3            | 7            | 3          | Problematic        | Problematic                           |
| Amines        | Ac <sub>2</sub> O      | 139     | 49      | H314                    | None | 3            | 7            | 3          | Problematic        | Problematic                           |
|               | Pyridine               | 115     | 23      | H302                    | None | 4            | 2            | 3          | Recommended        | Hazardous                             |
|               | TEA                    | 89      | -6      | H314                    | None | 6            | 7            | 3          | Problematic        | Hazardous                             |

<sup>a</sup> Only the highest scoring statements (*cf.* Table 1) are shown. The lowest figure is given when there is more than one statement in the highest scoring category, for the sake of simplicity. <sup>b</sup> HH: highly hazardous. <sup>c</sup> Solid at 20 °C.

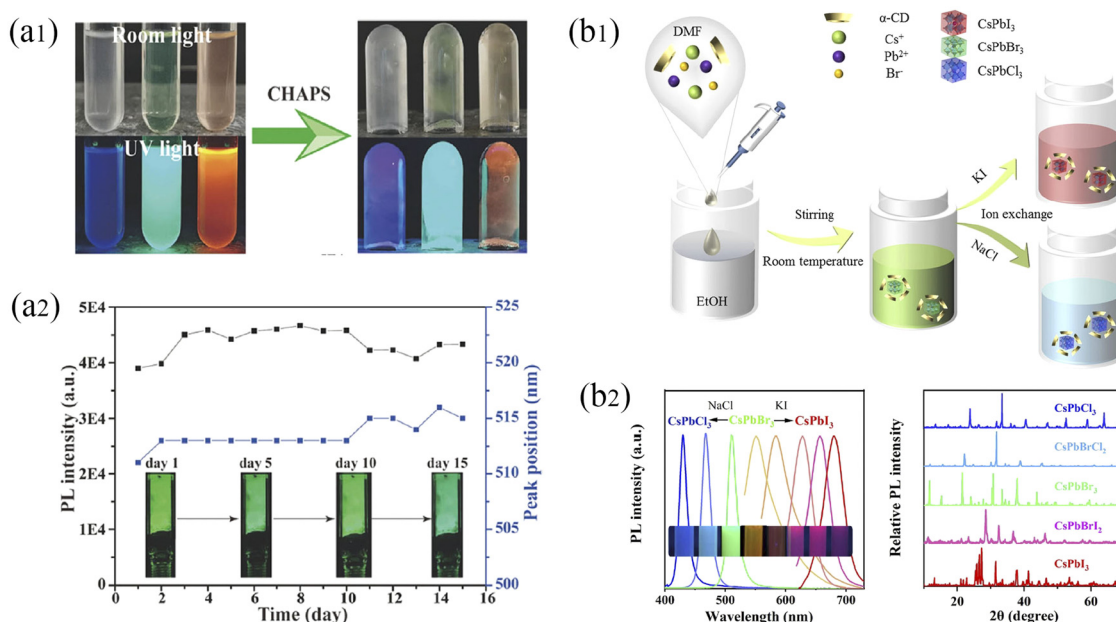
### 3. Low-toxicity solvents used in the preparation of precursor solutions

The CHEM21 data in Table 1 shows that water has an EHS score of 1, 1, and 1, which is the lowest score throughout the whole of Table 1. This indicates that water is the greenest solvent among the whole chemicals in the CHEM21 database. In the alcohol categorization, methanol (MeOH), ethanol (EtOH), isopropanol (IPA, also called i-PrOH), and ethyl acetate are the four popular solvents used in the preparation of precursor solutions. Among these chemicals, MeOH is hazardous to the human body with

an "H" score of 7, while EtOH and IPA are low-toxicity solvents with the same EHS data (3 for E, 3 for H, and 4 for S). Ethyl acetate has the same "E" and "H" scores as IPA, but a higher score of 5 for "S". Currently, these chemicals have been used in the preparation of the precursor solutions for perovskite materials as individual solvents or co-solvents. EtOH has been used as the solvent and antisolvent for the synthesis of PeNCs.

Using a co-solvent of H<sub>2</sub>O and EtOH, Zheng *et al.*<sup>36</sup> prepared CsPbBr<sub>3</sub> NCs under an ultrasonication process at room temperature. Note that the NC solution formed by the water-ethanol solvent can be transformed into a gel form with





**Fig. 1** (a) EtOH and H<sub>2</sub>O co-solvent for the synthesis of CsPbBr<sub>3</sub> NCs: (a1) optical images of colloidal PeNCs solutions transformed into gels by adding CHAPS, (a2) Time-dependent PL variations (black line: intensity, blue line: peak position). Reprinted with permission from ref. 36 Copyright (2021) Elsevier. (b) EtOH as an antisolvent for the preparation of CsPbX<sub>3</sub> (X = I, Br, Cl) NCs. (b1) Schematic of the synthesis of colloidal NCs and anion exchange of α-CD-capped perovskite (α-CD@CsPbBr<sub>3</sub> PeNCs) by ethanol, (b2) PL spectra (left) and XRD patterns (right) for the PeNCs. Reprinted with permission from ref. 37 Copyright (2023) the Royal Society of Chemistry.

enhanced PL (photoluminescence) stability after adding a chemical of zwitterionic 3-[(3-cholamidopropyl)-dimethylammonium]-1-propanesulfonate (CHAPS) (Fig. 1a). The CHAPS containing sulfonic group has a strong binding with surface Pb<sup>2+</sup> atoms of CsPbBr<sub>3</sub> NCs and acts as capping ligand to passivate surface defects of the NCs. For the same materials (CsPbBr<sub>3</sub> NCs), Zhang *et al.*<sup>37</sup> and Liang *et al.*<sup>38</sup> used EtOH as an antisolvent toward a green synthesis process. Adding the ligand of α-cyclodextrin (CD) led to the formation of α-CD@CsPbBr<sub>3</sub> with an average size of 35 nm and a PLQY (photoluminescence quantum yield) of 86.0%; the formed α-CD@CsPbBr<sub>3</sub> maintained in EtOH for 6 months only experienced a loss of less than 10% in luminescence.<sup>37</sup> Note that EtOH is a polar solvent, and an antisolvent is always a kind of non-polar solvent. In this case, the extraordinary application of EtOH as an antisolvent should be further investigated.

Fig. 1b presents a schematic of the formation and anion exchange of α-CD-capped perovskites. The PL spectra at the bottom of Fig. 1b are for well-synthesized NCs prepared by the anion exchange technique. It should be noted that the solubilities of various lead halides are different in EtOH, which may have difficulties for the anion exchange. However, the PL results in Fig. 1b are indicative of the feasibility of the anion exchange in an ambient environment. Similarly, silica-passivated CsPbBr<sub>3</sub> NCs with EtOH as an antisolvent exhibited a PLQY of ~80%.<sup>38</sup>

The preparation of precursor solution is a key step for the synthesis of nanocrystals. Green-route preparation of precursor solutions is of extreme significance to the synthesis of nanocrystals *via* a green approach. Ethyl acetate (EA) is frequently

used in the preparation of precursor solutions for solar cells. Jain *et al.*<sup>39</sup> fabricated lead-free bismuth based (CH<sub>3</sub>NH<sub>3</sub>)<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> perovskite-like solar cells *via* EA and achieved a power conversion efficiency (PCE) of 1.62% under 1 sun illumination. Wu *et al.*<sup>40</sup> used triethyl phosphate (TEP) as a solvent to obtain (FAPbI<sub>3</sub>)<sub>0.95</sub>(MAPbBr<sub>3</sub>)<sub>0.05</sub> NCs for solar cells with a PCE of 22.4%. IPA has been most used in antisolvent methods. For example, Liu *et al.*<sup>41</sup> used IPA as an anti-solvent and cetyltrimethylammonium chloride (CTAC) as an additive to prepare perovskite solar cells with a PCE of 23.4%. IPA also plays a role in passivating both surface and grain boundary defects, which offers an improvement in the PCE of corresponding solar cells. In addition to these commonly used green solvents, other ones have also been used in the preparation of precursor solutions, including diethyl carbonate<sup>32</sup> and isobutanol.<sup>42</sup>

Table 2 summarizes recent advancements in eco-friendly solvents. To date, green solvents have facilitated the synthesis of perovskite materials and associated devices *via* other paths, including interface engineering<sup>43</sup> and crystallization promotion.<sup>44</sup> All these reports indicate a multifunctional role of green solvents.

## 4. Green aqueous-solution methods

According to the CHEM21 data in Table 1, water (H<sub>2</sub>O) with the lowest EHS score is the greenest solvent for industrial manufacturing and biomedical applications. In the area of perovskite materials, green synthesis has been called for sustainable development from the view of commercialization and

Table 2 Recent advancements in eco-friendly solvents

| Material             | Role               | Structure   | Performance  | Ref. |
|----------------------|--------------------|-------------|--------------|------|
| EtOH                 | Precursor solution | NCs         | 38.1% (PLQY) | 36   |
| EtOH                 | Antisolvent        | NCs         | 86.0% (PLQY) | 37   |
| EtOH                 | Antisolvent        | NCs         | 80% (PLQY)   | 38   |
| EA                   | Precursor solution | Solar cells | 1.62% (PCE)  | 39   |
| EA                   | solution           | Solar cells | 22.37% (PCE) | 45   |
| TEP                  | Precursor solution | Solar cells | 22.4% (PCE)  | 40   |
| IPA                  | Antisolvent        | Solar cells | 23.4% (PCE)  | 41   |
| GBL/EtOH/acetic acid | Precursor solution | Solar cells | 23.4% (PCE)  | 27   |

industrialization.<sup>46–49</sup> Several H<sub>2</sub>O-based aqueous syntheses of PeNCs have been reported, and are discussed below.

#### 4.1 H<sub>2</sub>O + acid method

A typical aqueous method has been proposed to use DI (deionized) water and inorganic halogen acid, in which DI water is for the purpose of dissolving Cs-based saline halides and halogen acid for Pb-based saline halides. For the formation of PeNCs, except for the ligands such as oleylamine<sup>50</sup> and oleic acid,<sup>51</sup> dispersing agents and/or surfactants<sup>50</sup> are also used to enhance mono-dispersity and water-proof properties of PeNCs. For example, one of the water-proof molecules is fluorocarbon agent (FCA), which possesses extremely hydrophobic fluorocarbon chains with a low surface energy of –CF<sub>2</sub>– and –CF<sub>3</sub> groups<sup>52</sup> (lower surface energy normally typifies higher hydrophobicity<sup>35</sup>). Li *et al.*<sup>50</sup> employed perfluorooctyltriethoxysilane (C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, PFOTES) as FCA to synthesize CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> NCs. Generally, forming NCs needs antisolvents to lower the solubility of anion and cation in the precursor solution. In this work, they used an ice-water bath for the precipitation of perovskites (Fig. 2a). Ghosh and Kar used IPA and oleic acid as antisolvent and ligand respectively in the synthesis of Cs<sub>2</sub>AgBiCl<sub>6</sub> double perovskites (Fig. 2b).<sup>51</sup> This could be referred to as an organic-water medium for the precursor solution, in which IPA can bridge the water with hydrophilic –OH and the organic solvent with –CH<sub>3</sub> and has a moderate polarity (0.546<sup>53</sup>).

As an important part of perovskite materials, inorganic-organic hybrid PeNCs also draw wide attention in green synthesis. Here, we take MAPbX<sub>3</sub> (MA = CH<sub>3</sub>NH<sub>3</sub>, X = Cl, Br, I) as an example. Different from Cs-based perovskites, MA<sup>+</sup> is always from aqueous solution of CH<sub>3</sub>NH<sub>2</sub>. The synthesis of CH<sub>3</sub>NH<sub>2</sub>-based PeNCs is completed through the mixture of aqueous solution of CH<sub>3</sub>NH<sub>2</sub> and aqueous solution of PbX<sub>2</sub> (Fig. 2c). It needs to be pointed out that water can decompose perovskite crystals, so the pH of the aqueous solution is a crucial factor in controlling the formation of PeNCs. Geng *et al.* found that MAPbBr<sub>3</sub> powders prepared by DMF decomposed in pure water or aqueous solution of CH<sub>3</sub>NH<sub>2</sub> rapidly, but survived in small amounts of lead-halide complexes, such as [PbBr<sub>6</sub>]<sup>4–</sup>, in a low pH solution.<sup>54</sup> They inferred that [PbX<sub>6</sub>]<sup>4–</sup> complexes help to form PeNCs with a halide-rich surface and hinder the decomposition of the PeNCs in water, while H<sup>+</sup> (H<sub>3</sub>O<sup>+</sup>) and CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> cations from the solution on the surfaces of PeNCs maintain a suitable ion balance (Fig. 2c).<sup>54</sup> For the preparation of the same

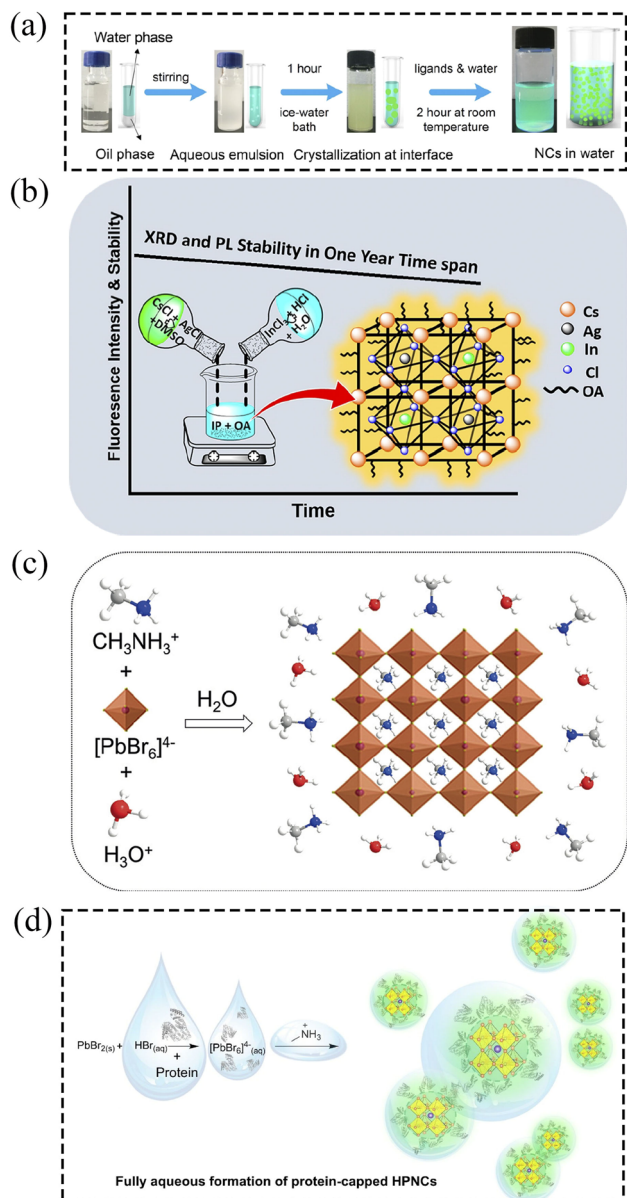
material of MAPbX<sub>3</sub> PeNCs, Aminzare *et al.* used protein (BSA) to stabilize the prepared PeNCs.<sup>55</sup> The protein, which functions as chains of amino acids linked by peptide bonds, provides a highly dynamic bonding environment to the PeNCs through hydrogen bonding,  $\pi$ – $\pi$ -stacking, van der Waals, and electrostatic interactions (Fig. 2d). As PeNCs are stored in an acid environment, the pH has a significant impact on the performance of the PeNCs, such as the PL intensity. In the BSA-modified PeNCs, the PL intensity was improved with the increase of pH from an overall profile. This indicates that a weaker acid solution can enhance the interaction between BSA and PeNCs.

Ligands play an important role in the formation and growth of PeNCs. Wei *et al.* used polyvinylpyrrolidone (PVP) as the ligand for the synthesis of MAPbBr<sub>3</sub> in an aqueous solution, where the interactive bonding between PVP with lactam groups enables the formation of PeNCs.<sup>56</sup> They demonstrated that the PL intensity of the PeNCs was dependent on the weight content of PVP, which suggests that an appropriate content of PVP can dramatically increase the PL intensity of the PeNCs and a low or overhigh content of PVP can cause the drop of the PL intensity of the PeNCs. Without PVP, the number of formed PeNCs was limited due to the anchoring failure of most monomers.

We note that DMF in the reported work of FCA-assisted synthesis of CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> NCs<sup>50</sup> was added in the synthesis process to accelerate the dissolving of Pb-based saline halides to obtain a precursor solution of high quality. Similarly, Ghosh *et al.* used an appropriate amount of DMSO for the dissolving of AgCl.<sup>51</sup> DMF and DMSO have been defined as harmful chemicals, which pose a serious threat to the environment and the health of human beings. Therefore, a greener approach needs to be developed. This is illustrated in the next section.

#### 4.2 Ultrasonication-assisted aqueous methods

**4.2.1 Halide acid as an additive in precursor solutions.** Due to the discrepancy of solubilities between Cs-based and Pb-based saline halides, there exists a limit to the complete dissolution of the two sorts of equimolar saline halides in DI water. Cs-Based saline halides have a large solubility in DI water, and Pb-based saline halides have a small solubility in DI water. Consequently, a small amount of halide acids is usually added into DI water for a thorough dissolving of the corresponding Pb-based saline halides. In general, the concentration of the halide acids should be as low as possible, to reduce the toxicity.



**Fig. 2** Schematic of the synthesis of perovskite nanocrystals with a halogen-cation-based aqueous solution and an inorganic halogen acid. (a) FCA-assisted synthesis of CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> PeNCs. Reprinted with permission from ref. 50 Copyright (2018) American Chemical Society. (b) IPA as an antisolvent for the synthesis of Cs<sub>2</sub>AgBiCl<sub>6</sub> double perovskites. Reprinted with permission from ref. 51 Copyright (2022) American Chemical Society. (c) Formation of MAPbBr<sub>3</sub> NCs in a low pH environment. Reprinted with permission from ref. 54 Copyright (2018) Wiley-VCH. (d) Protein-mediated MAPbBr<sub>3</sub> NCs. Reprinted with permission from ref. 55 Copyright (2022) American Chemical Society.

Tang *et al.* performed a series of aqueous syntheses of double perovskite NCs (DPNCs) *via* a two-step approach.<sup>57,58</sup> The first step is to synthesize double perovskite powder (DPP) in an aqueous solution by mixing Cs-based and Pb-based precursor solutions, followed by a heating process to evaporate the liquid in as-obtained powder (Fig. 3). The DPP is formed by a series of chemical reactions between cations and anions. The next step is the ultrasonication of the powder obtained in the

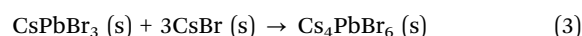
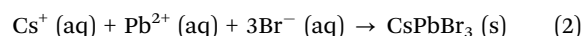
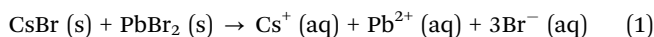
previous step to achieve nanosized perovskites. Note that ligands are indispensable for the formation of PeNCs. The role of ligands lies in saturating the dangling bonds to passivate the defects on the surface of PeNCs and encapsulating the PeNCs as surfactants to disperse the PeNCs in liquid solutions. Ligands also control the shapes of PeNCs in a dynamic environment where the bonding of ligands onto a crystal dominates the nucleation and growth kinetics of crystals.<sup>59,60</sup> That is, ligands have a surfactant-ligand duality effect on PeNCs. In the synthesis of PeNCs, the selection of ligands is critically important for the formation of PeNCs of high quality.

The most used ligands are oleylamine (OAm) and oleic acid (OA). Numerous experimental results have confirmed that PeNCs formed with combinational use of OAm and OA at a certain ratio exhibited superior performance in optoelectronic properties than the corresponding ones with an individual type of ligands on the surface. OA can serve as a single capping ligand but often is regarded as a reactant, since it participates in many ionic metathesis reactions. For instance, OA provides protons for the conversion of methylamine into methylammonium cations during the synthesis of MAPbI<sub>3</sub> NCs. It was found that the number of formed MAPbI<sub>3</sub> NCs is very low and the formed MAPbI<sub>3</sub> NCs are not stable if OA is absent.<sup>61</sup> Same situation is applied to OAm; bulk crystals are usually grown without amines.<sup>62</sup> It needs to be pointed out that the solubility of Pb-based saline halides in acid solutions is a key parameter for the formation of double-perovskite powder in the first step. Except for the acid concentration in the corresponding aqueous solution, temperature is another crucial factor determining the solubility of Pb-based saline halides.

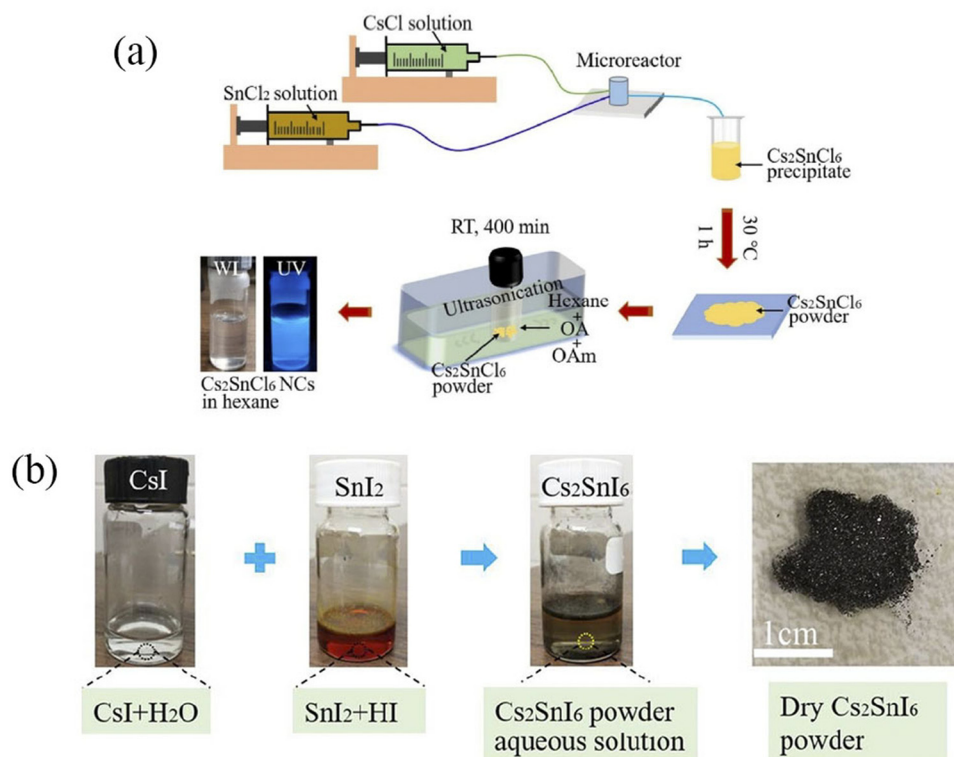
**4.2.2 Pure H<sub>2</sub>O method.** Even though the concentration of the halide acid used in the aqueous-based synthesis of PeNCs is low, it still causes mild harmfulness to the environment and the health of human beings. Pure water, a non-toxic, green solvent can completely address this concern. Tang *et al.*<sup>63,64</sup> demonstrated that using DI water as a sole solvent can produce perovskite powder first, and PeNCs are obtained through the ultrasonication of the perovskite powder in a nonpolar solvent with ligands for storage.

It is known that there is a huge difference in solubilities between CsBr and PbBr<sub>2</sub> in water. This indicates that it is difficult to use equimolar CsBr and PbBr<sub>2</sub> (or stoichiometric Cs<sup>+</sup>, Br<sup>+</sup>, and Pb<sup>2+</sup> in a molar ratio of 1 : 1 : 3) to form CsPbBr<sub>3</sub> in water. In fact, there are miraculous chemical reactions during the formation of CsPbBr<sub>3</sub> powder, which are discussed below.

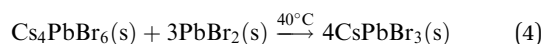
First, adding DI water to the mixture of equimolar CsBr and PbBr<sub>2</sub> powders achieves the formation of a white precipitate, consisting of Cs<sub>4</sub>PbBr<sub>6</sub> and PbBr<sub>2</sub>. The white precipitate reacts and forms brown CsPbBr<sub>3</sub> powder during a heating treatment. The whole process for the formation of CsPbBr<sub>3</sub> powder can be expressed by the following chemical reactions:<sup>63</sup>







**Fig. 3** Schematic of ultrasonication-assisted synthesis of perovskite materials in aqueous solutions. (a) Cs<sub>2</sub>SnCl<sub>6</sub> NCs. Reprinted with permission from ref. 57 Copyright (2022) the Royal Society of Chemistry. (b) Cs<sub>2</sub>SnI<sub>6</sub> powder. Reprinted with permission from ref. 58 Copyright (2023) American Chemical Society.



The fabrication process of the CsPbBr<sub>3</sub> powder is illustrated clearly in Fig. 4a–d. The critical element for the successful synthesis of the CsPbBr<sub>3</sub> powder is the material conservation before and after the reactions. In reaction (3), CsBr has a much higher solubility in water than PbBr<sub>2</sub> so CsPbBr<sub>3</sub> continuously reacts with superfluous CsBr to form Cs<sub>4</sub>PbBr<sub>6</sub>. As a result, superfluous PbBr<sub>2</sub> is left in the aqueous solution. The equilibrium then drives the chemical reaction to move in the direction of the material conservation. That is, Cs<sub>4</sub>PbBr<sub>6</sub> reacts further with PbBr<sub>2</sub> to achieve the final product of CsPbBr<sub>3</sub>.

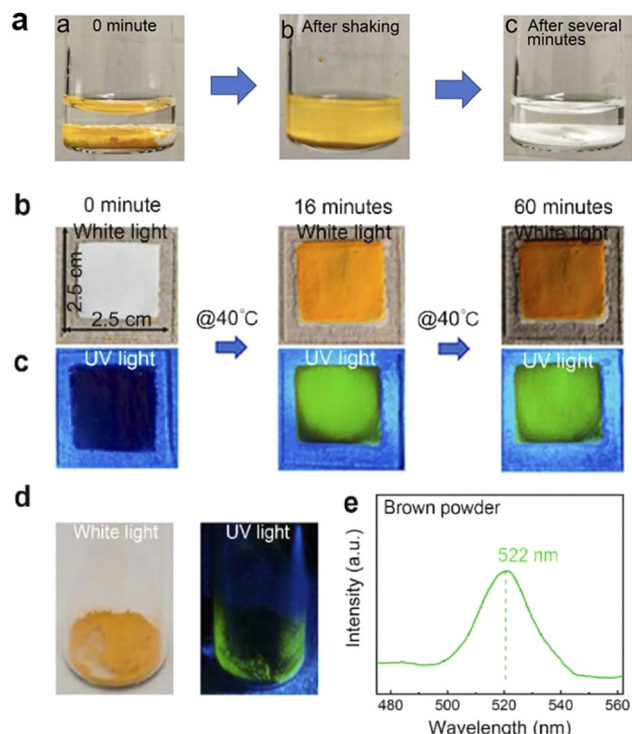
The next step is to synthesize CsPbBr<sub>3</sub> NCs from the as-prepared CsPbBr<sub>3</sub> powder. Note that this process was conducted in an ultrasonic bath, and the powder was placed in a container with a nonpolar solvent and ligands. Perovskite materials including powder and NCs have a super low solubility in nonpolar solvents, so the final product can be stored and saved in nonpolar solvents. It is also noted that suitable ligands are indispensable in the formation of NCs and are needed to reach monodisperse NCs of high quality in the corresponding solvent. No NCs can be formed without ligands.

#### 4.2.3 Impact of ultrasonication time on the size of PeNCs.

Ultrasonication, which involves the propagation of high-frequency acoustic waves, has been considered as a green approach to synthesize NCs. The acoustic energy absorbed by semiconductor particles can cause the formation and growth of

cracks, leading to the breakage of the particles when the cracks grow through the particles. This trend leads to the disintegration of particles of larger sizes to the ones of smaller sizes,<sup>65</sup> as illustrated in Fig. 5a and 6. Note that the force on a particle due to ultrasonic wave is proportional to the volume of the particle, thus resulting in an increase in the number of smaller particles and the concentration of NCs generally with an increase in the ultrasonication time. The concentration of NCs will reach a maximum due to the saturation of NCs in the solution, as evidenced by the optical characteristics of the NCs in Fig. 5b–d. This trend indicates that an appropriate ultrasonication duration is critical to the yield of NCs because a longer ultrasonication duration (which is beyond the saturation point) will not contribute to the production of more NCs. Note that the ultrasonication was carried out in an ultrasonic bath, in which the container with large particles inside was placed to obtain NCs.

Another method for the fabrication of NCs uses an ultrasonication probe or tip. In this method, the ultrasonication probe is inserted into the solution with precursor powders and the vibration energy from the probe breaks the powders into NCs. To be an efficient way, beads, strikingly colliding with perovskite precursors upon exposure to ultrasound, are added to the solution.<sup>66</sup> It was demonstrated that ultrasonication with beads achieved a remarkable enhancement in the yield of PeNCs over the one without beads. Nevertheless, debris from the beads is likely produced and presented in the NC solution,



**Fig. 4** Optical images showing the synthesis process of CsPbBr<sub>3</sub> powder. (a) Equimolar CsBr and PbBr<sub>2</sub> mixed in DI water. (b) and (c) Synthesis of CsPbBr<sub>3</sub> powder film achieved by heating. (d) CsPbBr<sub>3</sub> powder was removed from the glass substrate. (e) PL spectrum of as-obtained CsPbBr<sub>3</sub> powder. Reprinted with permission from ref. 63 Copyright (2021) Elsevier.

leading to the contamination of the formed PeNCs. Such an issue is similar to the ball-milling method. It needs to be pointed out that continuous ultrasonication can cause an increase of temperature, which may impact the optical characteristics of the formed PeNCs due to the temperature dependence of the photoemission of PeNCs.<sup>64,67–69</sup> On the other side, the method with an ultrasonication probe immersed in the precursor solution may require the use of an open-ended container to limit structural damage to the container. This can cause the loss of organic solvent through evaporation.

Some aspects need to be noted in the preparation of PeNCs with ultrasonication probes. First, the yield of PeNCs will be reduced because most nonpolar solvents as antisolvents are volatile and can easily evaporate out of the precursor solutions with precursor cations and anions if open-ended containers are used. As a result, a sealed system is needed. Secondly, the dust in the air can fall into the PeNC solution if no sealed structure is used. Finally, the container can experience breakage if the ultrasonication power is higher than the safety limit. Therefore, it is very important to select a reasonable ultrasonication-based method for the synthesis of PeNCs, and more efficient and reliable systems need to be developed for the ultrasonication-based methods.

It is worth mentioning that microwaving is also a path that can be used for the synthesis of PeNCs. Long *et al.*<sup>70</sup> used

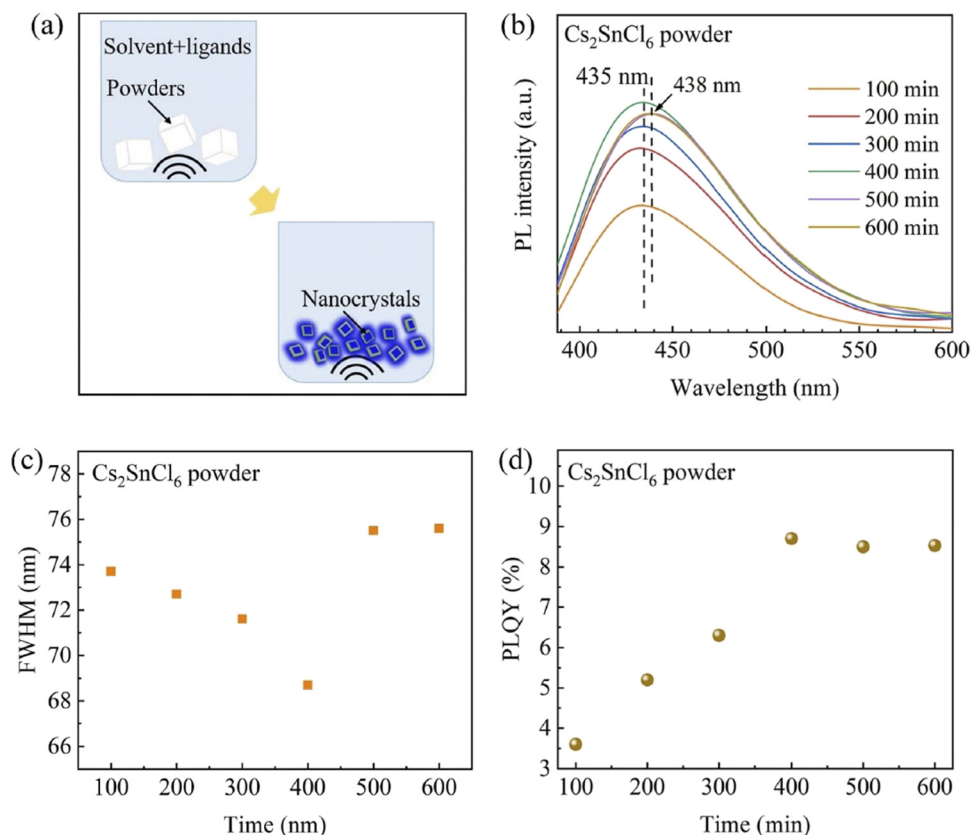
1-octadecene (ODE), OA, OAm, PbX<sub>2</sub> (X = Cl, Br, I) and Cs<sub>2</sub>CO<sub>3</sub> as precursor sources to synthesize CsPbBr<sub>3</sub> NCs in a household microwave oven, achieved a PLQY of 92.17% for the prepared PeNCs. Using a similar strategy, Li *et al.*<sup>71</sup> produced CsPbBr<sub>3</sub> NCs in a microwave oven and found an increase of the PL intensity with increasing the radiation time of the microwave. In contrast to the approach used by Long *et al.*,<sup>70</sup> they separated the Cs source and the Pb source by placing the two different materials (the Cs source and the Pb source) at two opposite ends of a quartz boat, instead of mixing the two precursor sources together, and collected intermediate reaction products with a suitable power of the microwave. Obviously, microwaving provides a green approach for the synthesis of PeNCs and has potential to achieve large-scale manufacturing at low cost. However, the reactions between the Cs source and the Pb source may not be sufficient to completely produce the final product of PeNCs.

**4.2.4 Impacts of post-treated ligands on the size and optical properties of PeNCs.** Solvent, surface ligands and/or surrounding medium play important roles in limiting aggregation of NCs due to the interaction between NCs. The methods used to add ligands into solutions can be different. Most methods add ligands in precursor solutions prior to the formation and nucleation of crystals, such as the HI and anti-solvent methods. However, ligands can also be added after the formation of crystals in ultrasonication-assisted methods.<sup>57,58,63,64</sup> This indicates that there exists a subtle interaction between ligands and NCs.

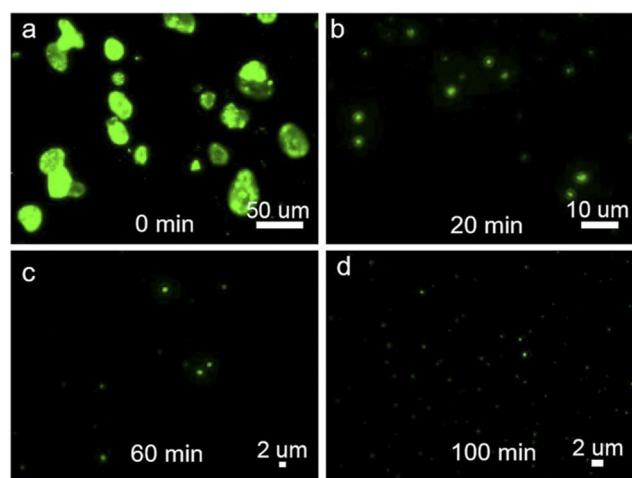
In the HI method, Cs-oleate and PbX<sub>2</sub> (X = Cl, Br, I) react to produce CsPbX<sub>3</sub> NCs and byproducts of Pb-oleate and oleyl ammonium bromide (OAmH-Br), and OAmH-X is preferably bound to PeNCs instead of Pb-oleate. The results from the Nuclear Magnetic Resonance (NMR) analysis revealed that OAmH-X acts as an X-type ligand bonding to the surface of PeNCs. Specifically, anions coordinate to Cs<sup>+</sup> and Pb<sup>2+</sup> on the surface of PeNCs, and OAmH<sup>+</sup> cation bonds to X<sup>-</sup> of PeNCs.<sup>72</sup> In contrast, the NMR results suggest that oleate strongly bonds to undercoordinated Pb and Cs atoms in the antisolvent method, and OAm binds weakly to surface protons and uncoordinated Pb.<sup>73</sup>

The amounts of ligands have a remarkable influence on the sizes of the perovskites post-treated with the ligands. Let us use the ratio of OA to OAm as an example. Tang *et al.*<sup>57</sup> found the dependence of the size and optical properties of Cs<sub>2</sub>SnCl<sub>6</sub> NCs on the ratio of the ligands used in the solution. Changing the ratio of OA to OAm from 40:10 to 10:40 caused the blueshift of the PL peak to 429 nm from 435 nm, indicating a decrease in the size of Cs<sub>2</sub>SnCl<sub>6</sub> NCs. Also, decreasing the ligand ratio led to a decrease of the PL intensity (Fig. 7a) (with a broadening full width at half maximum as shown in Fig. 7b), PLQY (Fig. 7c), and lifetime (Fig. 7d). Similarly, double perovskite Cs<sub>2</sub>SnI<sub>6</sub> NCs were derived from the powder counterpart.<sup>58</sup> These results demonstrate the successful synthesis of NCs by the novel method of post-treatment ligands, which can be attributed to the interaction/bonding between ligands and NCs to enable the attachment of ligands onto NCs. However, the mechanisms of





**Fig. 5** Effect of ultrasonication time on optical characteristics of  $\text{Cs}_2\text{SnCl}_6$  DPNCs. (a) Schematic of the ultrasonication process. (b) PL spectra for different ultrasonication times. (c) FWHM of the PL spectra. (d) PLQY of  $\text{Cs}_2\text{SnCl}_6$  DPNCs. Reprinted with permission from ref. 57 Copyright (2022) the Royal Society of Chemistry.



**Fig. 6** Fluorescent images of  $\text{CsPbBr}_3$  powders in toluene for different ultrasonication durations. Reprinted with permission from ref. 63 Copyright (2021) Elsevier.

how ligands are attached to NCs remain elusive and need to be explored in the future.

The PLQY enhancement of PeNCs can be generally attributed to the quantum size (confinement) effect, which occurs when the characteristic size (diameter) of PeNCs is comparable

to or smaller than the exciton Bohr radius of the corresponding bulk semiconductor.<sup>22,74–76</sup> Tang *et al.*<sup>58</sup> proposed a critical characteristic size ( $a_c$ ) to describe a similar phenomenon. If the characteristic size of a crystal is larger than  $a_c$ , the bandgap of the crystal is not tuneable by changing the crystal size, *i.e.*, the size (confinement) effect will disappear. Here,  $a_c$  is expressed as<sup>58</sup>

$$a_c = \left( \frac{3\hbar^2 \pi^2 \ln(m/m_e^*)}{4mk_B T} \right)^{1/2}$$

in which  $\hbar$  is the reduced Planck constant;  $m$  and  $m_e^*$  are the mass and reduced effective mass of an electron, respectively; and  $k_B$  and  $T$  are Boltzmann's constant and the absolute temperature, respectively.

There are reports that the morphology of PeNCs can be dependent on surrounding material, such as polymers. Xiao *et al.*<sup>77</sup> reported the change in the size of  $\text{CsPbBr}_3$  NCs with the change in the amount of carboxylic-based polymer (polymer ligands). They found that increasing the amount of the polymer ligands reduced the size of  $\text{CsPbBr}_3$  NCs and caused a blue shift of the PL peak wavelength from green (519 nm) to blue (446 nm) (Fig. 8a). They attributed this behavior to the shearing of the polymer ligands<sup>77</sup> and also observed the change of the shape of  $\text{CsPbBr}_3$  NCs from a cubic-like shape to a cylindrical-

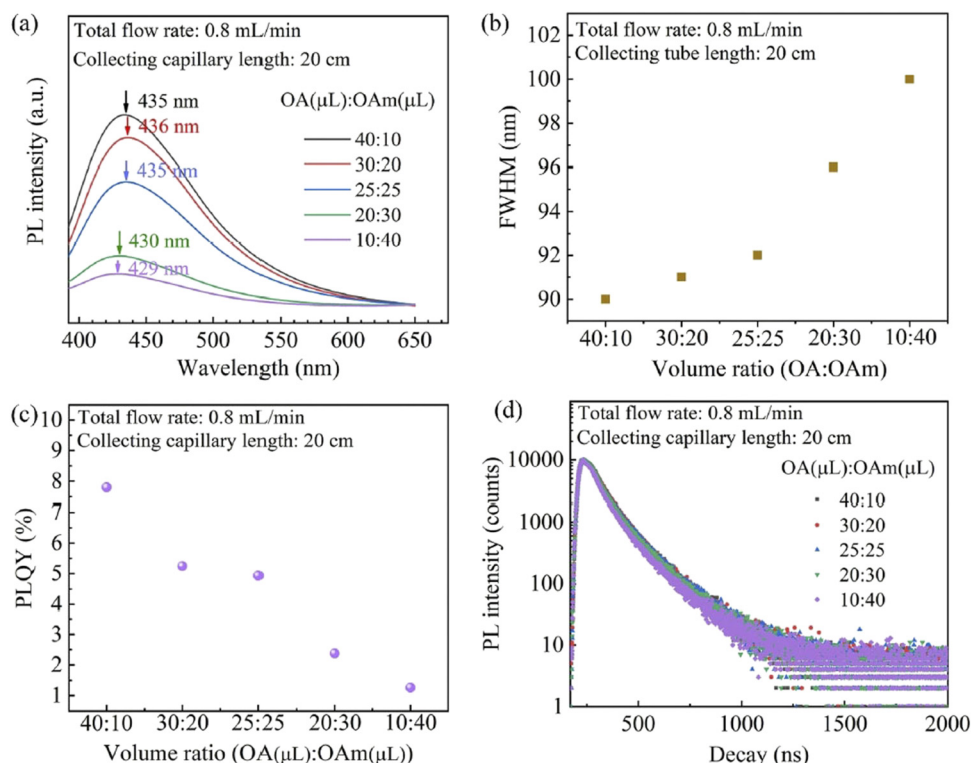


Fig. 7 Effect of the ratio of OA to OAm on optical properties of Cs<sub>2</sub>SnCl<sub>6</sub> DPNCs. (a) PL intensity. (b) FWHM of the PL spectra. (c) PLQY. (d) Lifetime. Reprinted with permission from ref. 57 Copyright (2022) the Royal Society of Chemistry.

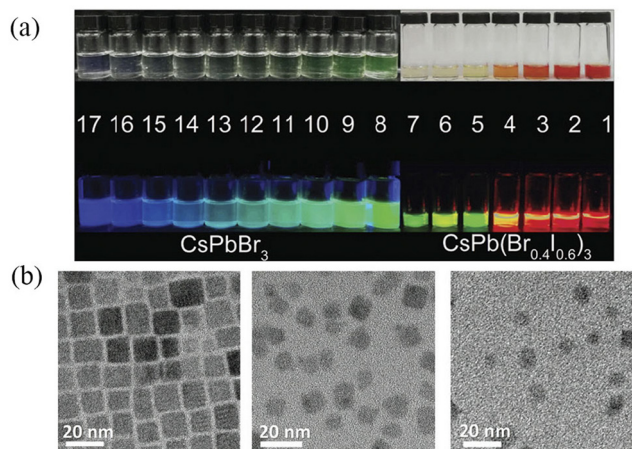


Fig. 8 Effects of the amount of polymer ligands on the size (a) and morphology (b) of CsPbBr<sub>3</sub> PeNCs. Reprinted with permission from ref. 77 Copyright (2020) the Royal Society of Chemistry.

like shape (Fig. 8b). They did not discuss the reason for this phenomenon. We suggest that the shape change of the CsPbBr<sub>3</sub> NCs may be attributed to the role of the interface energy between the polymer ligands and the NCs, because interfacial energy can affect the arrangements of atoms on the surface of NCs.<sup>35</sup> Also, there exists interface stress between NCs and matrix (polymer ligands).<sup>78</sup> The interface stress can be considered as internal stress, which plays a role in the stress state and optical properties of NCs.<sup>78</sup>

Table 3 summarizes the optical characteristics of PeNCs prepared by aqueous methods. Note that the difficulty of obtaining the effective electron mass ( $m_e^*$ ) of a semiconductor at a temperature makes it a challenge to determine the dependences of the quantum confinement size of various PeNC on crystal structures and compositions. The sizes in Table 3 are experimental results.

It needs to be pointed out that doping is an effective strategy to significantly improve the optical properties of PeNCs. Tan *et al.* reported an enhanced PLQY of Cs<sub>2</sub>SnCl<sub>6</sub> by Bi doping.<sup>79</sup> The originally nonluminous Cs<sub>2</sub>SnCl<sub>6</sub> emits a deep-blue light of 455 nm with the Bi doping, and the PLQY increases to ~80% from 0%. They also found that the PLQY and wavelength can be tuned by the Bi amount remarkably. For example, Bi content of 0.11% resulted in a PLQY of 67.6% and Bi of 2.75% led to a 78.9% in PLQY for Cs<sub>2</sub>SnCl<sub>6</sub>. These results indicate doping engineering likely is a highly efficient strategy to enhance the optical properties of PeNCs.

There have been reports in doping engineering, which can be categorised into organic doping<sup>80–85</sup> and inorganic doping.<sup>86–91</sup> These doping methods have been widely used in boosting the performance of perovskite devices.<sup>82,86</sup>

### 4.3 Strategy for structural stability in aqueous environments

The structural stability of PeNCs under ambient conditions and/or operation conditions is a major challenge for the applications of PeNCs. Both moisture and oxygen can attack halide perovskites through grain boundaries and surfaces,

Table 3 Summary of optical characteristics of PeNCs prepared by aqueous methods

| Material                                               | Solvent                                       | Antisolvent | Size (nm) | PLQY (%) | Ref. |
|--------------------------------------------------------|-----------------------------------------------|-------------|-----------|----------|------|
| CsPbBr <sub>3</sub>                                    | H <sub>2</sub> O + EtOH                       | —           | 14.5      | ~38.1    | 36   |
| α-CD@CsPbBr <sub>3</sub>                               | DMF                                           | EtOH        | ~35.0     | ~33.4    | 37   |
| Silica@CsPbBr <sub>3</sub>                             | ODE                                           | EtOH        | —         | ~80      | 38   |
| CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> | HBr + DMF                                     | FCAs        | 20–100    | ~80      | 50   |
| CsPbBr <sub>3</sub> /CsPb <sub>2</sub> Br <sub>5</sub> | HF aqueous                                    | —           | ~110      | 77       | 92   |
| MAPbBr <sub>3</sub>                                    | HBr + CH <sub>3</sub> NH <sub>2</sub> aqueous | —           | —         | ~40      | 54   |
| MAPbBr <sub>3</sub>                                    | H <sub>2</sub> O                              | —           | ~5        | ~94      | 64   |
| CsPbBr <sub>3</sub>                                    | H <sub>2</sub> O                              | —           | ~5, 200   | ~17, 80  | 63   |
| Cs <sub>2</sub> SnCl <sub>6</sub>                      | HCl aqueous                                   | —           | ~2.5      | ~13.4    | 57   |
| Cs <sub>2</sub> SnI <sub>6</sub>                       | HI aqueous                                    | —           | ~4        | ~7.4     | 58   |
| Bi:Cs <sub>2</sub> SnCl <sub>6</sub>                   | HCl aqueous                                   | —           | —         | 78.9     | 79   |
| Cs <sub>2</sub> AgInCl <sub>6</sub>                    | DMSO + HCl aqueous                            | —           | 17.76     | —        | 51   |
| MAPbBr <sub>3</sub> @PbBr(OH)                          | H <sub>2</sub> O                              | —           | ~60       | 75.26    | 93   |

leading to the loss of functionality and the decomposition of halide perovskites.<sup>94,95</sup> The detachment of ligands from the surface of PeNCs in the air can increase the number of defects in PeNCs, which become the preferential sites for the attack of moisture and oxygen. Enormous efforts have thus been devoted to enhancing the stabilities of PeNCs with the use of moisture-tolerance capping over the past years.

One common method is to encapsulate NCs with a shell as a passivation layer, such as polymers, semiconductors, *etc.* Polymers as capping shells to protect the core of NCs were proposed and demonstrated. Wei *et al.*<sup>96</sup> used a swelling–shrinking strategy to prepare CsPbBr<sub>3</sub>@polystyrene nano/micron beads and achieved an enhancement to the resistance of water and a high quantum efficiency. The CsPbBr<sub>3</sub> NCs were embedded into polystyrene, which effectively prevented NCs from the attack of environmental elements, such as water, oxygen, *etc.*, with hydrophobic polymer chains. Using a similar strategy, Zhang *et al.*<sup>97</sup> embedded CsPbX<sub>3</sub> (X = Cl, Br, I) NCs into micro-hemispheres (MHS) of polystyrene to improve the resistance to water. The as-synthesized NCs@MHSSs, which were washed three times, exhibited excellent optical performance in water. The NCs@MHSSs were used as luminescence probes in the tagging of 264 macrophages, which demonstrated potential applications in biomedical engineering.

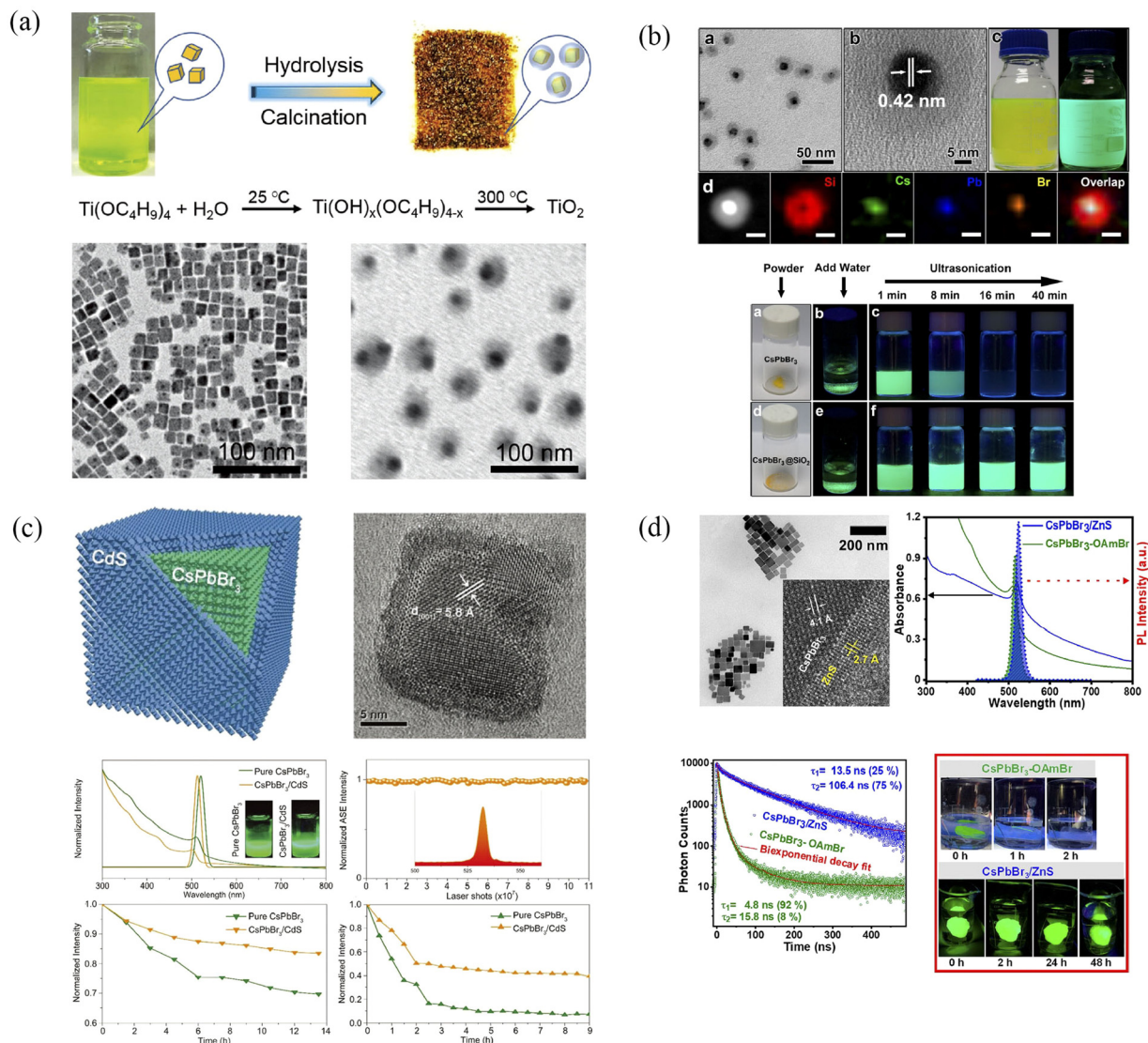
Although the enhanced environmental stability and the water-proof quality of PeNCs have been realized with a polymer shell on the surface of PeNCs, the polymer shell fails to achieve a compact encapsulation for the core of PeNCs. This can cause easy detachment of the polymer shell from the surface of PeNCs. Also, most polymer shells are insulators, which can significantly hinder the charge transports between PeNCs and between the hole/electron transport layer and PeNCs. This can significantly impair the performance of PeNC-based optoelectronic devices and systems. Alternatively, inorganic shells can likely solve these problems to some extent. Most inorganic materials have low solubilities in aqueous solutions, and some inorganic shells can be formed on the surface of PeNCs *via* heterogeneous epitaxial growth. These features enable inorganic shells more robust to resist the attack from water molecules.

Li *et al.* prepared CsPbBr<sub>3</sub>@TiO<sub>2</sub> core–shell nanoparticles, which exhibited superior water stability, structural stability and

optical stability over three months.<sup>98</sup> The synthesis of the core–shell NCs was achieved through a two-step process. The CsPbBr<sub>3</sub> NCs were firstly prepared by a hot injection method, and the CsPbBr<sub>3</sub>@TiO<sub>2</sub> core–shell nanoparticles were then fabricated *via* hydrolysis and calcination (Fig. 9a). Note that the calcination process needs a high temperature of 300 °C, which is energy-consuming. An alternative way is called for low temperatures. Zhong *et al.* proposed a one-pot approach to obtain CsPbBr<sub>3</sub>@SiO<sub>2</sub> core–shell nanoparticles at room temperature (30 °C).<sup>99</sup> The shell layer of SiO<sub>2</sub> was formed by adsorbing silica oligomers derived from the hydrolysis of tetramethoxysilane (TMOS). With the SiO<sub>2</sub> shell, the CsPbBr<sub>3</sub> NCs displayed distinct stability against water compared to pure CsPbBr<sub>3</sub> NCs (Fig. 9b). However, it needs to be pointed out that SiO<sub>2</sub> has a high resistance to the charge transport in optoelectronic devices especially in vertical-structured devices, such as LEDs, photodetectors, and solar cells, in which electrons transport between the electron transport layer and NCs. In this case, SiO<sub>2</sub>-coated core–shell PeNCs have an inferior optoelectronic performance even though they possess superior environmental stability. Therefore, seeking suitable semiconductors as shells is a critical step in the development of high-stable PeNCs for optoelectronic devices and systems of high-performance.

Imitating the successful synthesis of II–VI core–shell NCs, Tang *et al.* successfully prepared CsPbBr<sub>3</sub>/CdS core/shell QDs (quantum dots) with CdS as the shell layer (Fig. 9c).<sup>100</sup> The CdS layer significantly depressed the blinking and instability of the core of CsPbBr<sub>3</sub> NCs. Auger non-radiative recombination was suppressed through bandgap engineering. The core–shell NCs exhibited superior humidity and thermal stabilities over pure CsPbBr<sub>3</sub> NCs. However, toxic Cd-based saline chemicals are detrimental to the environment and the health of human beings. Cd-free NCs have been gaining more attention and will be mainstream in terms of commercialization. Driven by this effort, Ravi *et al.*<sup>101</sup> replaced CdS with toxicity-mitigating ZnS to fabricate CsPbBr<sub>3</sub>@ZnS core–shell NCs with electrons being confined inside the core and holes being delocalized over both the core and shell (Fig. 9d). The CsPbBr<sub>3</sub>@ZnS core–shell NCs exhibited significant improvement in the carriers' lifetime and water stability, compared to the CsPbBr<sub>3</sub> NCs without ZnS shells. The improvement can be attributed to the passivation





**Fig. 9** (a) CsPbBr<sub>3</sub>@TiO<sub>2</sub> core-shell NCs: schematic for the synthesis (top) and TEM images (bottom) of pure and core-shell NCs. Reprinted with permission from ref. 98 Copyright (2018) Wiley-VCH (b) CsPbBr<sub>3</sub>@TiO<sub>2</sub> core-shell NCs: (top) TEM and optical images and (bottom) stability in water. Reprinted with permission from ref. 99 Copyright (2018) American Chemical Society. (c) CsPbBr<sub>3</sub>@CdS core-shell NCs: (top) TEM image and (bottom) the humidity and thermal stability tests. Reprinted with permission from ref. 88 Copyright (2019) Wiley-VCH. (d) CsPbBr<sub>3</sub>@ZnS core-shell NCs with TEM images, optical characteristics versus pure NCs and the water stability test. Reprinted with permission from ref. 89 Copyright (2020) American Chemical Society.

of defects with the ZnS shell for the core of CsPbBr<sub>3</sub> NC. These investigations highlight the potential applications of core-shell PeNCs in the new-generation optoelectronic devices and systems with long-term structural and optical stabilities. The results underline that the improvement of the structural stability of core/shell PeNCs under aqueous environments can be realized by the growth of a shell layer of water-proof inorganic material on the surface of core material, especially, the successful formation of a Cd-free shell layer of ZnS on the core material of CsPbBr<sub>3</sub>. This makes it a promising green route to boost their aqueous stability.

## 5. Conclusions and perspectives

There is no doubt that green manufacturing of PeNCs has huge potential for their future industrialization. PeNCs have

exhibited tremendous prospects in the fields of lighting and display due to their outstanding optoelectronic properties. However, the production of PeNCs still relies on the use of organic solvents, which hinders their further industrialization from a sustainable viewpoint. This Feature Article has discussed green solvents used so far for the synthesis of PeNCs, mainly focusing on aqueous methods. However, there are still several challenges faced for their green manufacturing.

### Green ligands for capping

For the synthesis of PeNCs, the commonly used ligands are toxic, including OA and OAm. Even though some green polymers including protein have been used as a capping layer for the preparation of PeNCs, their PLQYs are much lower than the ones prepared with OA and OAm. Consequently, the use of

green ligands is crucial for the realization of green manufacturing of PeNCs, which however remains a challenge. It needs to be pointed out that the compatibility between ligands and solvents should be considered in the synthesis of PeNCs. This is because the compatibility between ligands and solvents plays an important role in producing PeNCs of high-quality. For example, H<sub>2</sub>O is now the greenest solvent and has been used for the fabrication of PeNCs successfully. However, the organic ligands of OA and OAm cannot coexist in aqueous systems, and the separation of OA and OAm from H<sub>2</sub>O is present in aqueous solutions. EtOH is considered as a green solvent and can be mutually soluble in water and most organic solvents, and EtOH has good compatibility with OA and OAm. The deficiencies lie in the PLQY of the PeNCs prepared with EtOH, which is inferior to the ones with toxic solvents of DMF and DMSO. Efforts are suggested to be engaged in these aspects in future studies.

### Interface engineering for aqueous stability

Environmental instability is a long-term issue for PeNCs because the defects of PeNCs are susceptible to the attacks of H<sub>2</sub>O and O<sub>2</sub> molecules, *etc.* To date, several approaches have been proposed to improve the aqueous stability of PeNCs, such as polymer capping, TiO<sub>2</sub>-based, CdS-based, ZnS-based core-shell structures, *etc.* The highest PLQY of these core-shell PeNCs had reached ~90%, which is comparable to pure PeNCs. Aqueous solutions as a non-toxic or low-toxic medium are preferable for the storage of PeNCs to mitigate the detrimental effects of organic solvents on the environment. The great aqueous stability of core-shell PeNCs allows for the use of aqueous solutions for their storage and can contribute to their air stability and device stability.

Generally, it requires the use of ligands on PeNCs in order to hinder the agglomeration of PeNCs in liquid solutions, including aqueous solutions. Green ligands need to be developed for the dispersing of PeNCs in liquid solutions. This elicits another issue on the efficiency of PeNC-based devices. Currently, the efficiency of PeNC-based devices with the PeNCs prepared by green solvents is much lower than the corresponding ones with the PeNCs prepared by conventional toxic solvents. The main reason goes to the quality of the PeNCs, including PLQY, stability, crystallinity, *etc.* Device encapsulation can also impact the performance of PeNCs. Effective encapsulation can greatly improve the performance of PeNCs and the efficiency of devices because light extraction can be boosted with effective strategies. In addition, the quenching of light emission can occur during normal operation conditions due to the release of heat and the decomposition of PeNCs. Heat management should be an effort-dedicated topic for the improvement of devices' lifetime.

### Mechanical reliability of PeNCs and devices

One of the concerns on the applications of PeNCs is mechanical stability which affects the performance of the associated devices and systems. Carrier's mobility in semiconductors decreases generally with increasing tensile stress and pressure

because the nucleation and growth of cracks and/or defects can appear under mechanical stress. In particular, stress can also result in changes in the bandgap of PeNCs, which affects the wavelengths of light emission. For devices, such as LEDs, the shift in the emission wavelength of LEDs can cause the distortion of images in display fields. In this regard, it is of practical importance to investigate the mechanical stability of PeNCs and the associated devices under a variety of environments and operating conditions.

Currently, there are some reports focusing on the mechanical stability of perovskite materials and devices. However, more studies are needed to understand the environmental and operating effects as well as the effects of external stimuli, including mechanical deformation, on the mechanical stability of PeNCs prepared by green-route manufacturing. Especially, the mechanical stability of PeNCs plays an important role in the structural integrity of flexible optoelectronic devices and systems, which consist of multilayer structures, including an electron transfer layer, perovskite layer, and hole transport layer. The recurrent bending, folding, stretching and/or twisting can likely cause the degradation/damage of individual layers and PeNCs and lead to the malfunction and failure of devices and systems. Systematical studies of the effects of mechanical deformation on the structural stability of PeNCs under a variety of environments are highly desirable.

Devices and systems under operating conditions will generate heat, which affects not only the stability of PeNCs but also the performance of the associated devices and systems. High temperature can cause serious quenching to optical characteristics of PeNCs, such as PL, since PeNCs can experience decomposition and/or phase transition at elevated temperatures. This can undermine the functionality of the devices and systems, including solar cells, photodetectors, and so forth. Also, thermal expansion always occurs with increasing temperature, which results in volumetric changes and causes structural instability of PeNCs and the associated devices and systems. There exists thermomechanical interaction, which plays a role in the performance of PeNCs and the functionality of the associated devices and systems under operating conditions and at elevated temperatures. In addition, the passivation of defects is increasingly becoming mainstream to improve the mechanical stability of PeNCs and the associated devices and systems. There is a great need to understand the effects of thermomechanical interaction on the structural stability of PeNCs in a variety of materials under external stimuli.

PeNCs have already been proven to be promising materials, which have attracted great interest in multi-fields to explore conspicuous experimental workflows for sustainable manufacturing and for developing feasible and reliable systems to understand the thermal-mechanical-optical coupling in PeNCs. The comprehensive understanding of the thermal-mechanical-optical coupling in PeNCs and the development of sustainable manufacturing will allow for the industrialization of the green manufacturing of PeNCs of high quality and the improvement of the structural integrity and performance of PeNC-based devices and systems. These efforts will contribute to meaningful progress

in addressing the challenges highlighted in this Feature article and forward the sustainability and durability of the promising green technology for the manufacturing of PeNCs.

## Conflicts of interest

There are no conflicts to declare.

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## References

- R. A. Sheldon, *ACS Sustainable Chem. Eng.*, 2018, **6**, 32–48.
- R. A. Sheldon, *Green Chem.*, 2017, **19**, 18–43.
- R. A. Sheldon, *Chem. Soc. Rev.*, 2012, **41**, 1437–1451.
- A. Sahu and D. Kumar, *J. Alloys Compd.*, 2022, **924**, 166508.
- D. Vasudevan, R. R. Gaddam, A. Trinchi and I. Cole, *J. Alloys Compd.*, 2015, **636**, 395–404.
- D. Yang, D. Wang, X. Fang, D. Fang, L. Yang, C. Xiang, J. Li and X. Wang, *Laser Optoelectron. Progress*, 2023, **60**, 1500004.
- S. Liu, M. Wang, X. Yu, H. Li, H. Lu, X. Wen, M.-Y. Li and J. Zhang, *Adv. Opt. Mater.*, 2023, DOI: [10.1002/adom.202301252](#).
- R. Schwanninger, S. M. Koepfli, O. Yarema, A. Dorodnyy, M. Yarema, A. Moser, S. Nashashibi, Y. Fedoryshyn, V. Wood and J. Leuthold, *ACS Appl. Mater. Interfaces*, 2023, **15**, 10847–10857.
- Y.-H. Won, O. Cho, T. Kim, D.-Y. Chung, T. Kim, H. Chung, H. Jang, J. Lee, D. Kim and E. Jang, *Nature*, 2019, **575**, 634–638.
- P. Yu, S. Cao, Y. Shan, Y. Bi, Y. Hu, R. Zeng, B. Zou, Y. Wang and J. Zhao, *Light: Sci. Appl.*, 2022, **11**, 162.
- A. Fakharuddin, M. K. Gangishetty, M. Abdi-Jalebi, S.-H. Chin, A. R. B. M. Yusoff, D. N. Congreve, W. Tress, F. Deschler, M. Vasilopoulou and H. J. Bolink, *Nat. Electron.*, 2022, **5**, 203–216.
- C. Mao, S. Ju, J. Zheng, Y. Zheng, Z. Xu, L. Lin, H. Hu, K. Yang, T. Guo and F. Li, *Adv. Opt. Mater.*, 2023, **11**, 2202058.
- Y. Han, X. Chang, X. Cheng, Y. Lin and B.-B. Cui, *Laser Photonics Rev.*, 2023, **17**, 2300383, DOI: [10.1002/lpor.202300383](#).
- Y. Zhang, Y. Li, X. Xin, Y. Wang, P. Guo, R. Wang, B. Wang, W. Huang, A. J. Sobrido and X. Li, *Nat. Energy*, 2023, **8**, 504–514.
- H. Huang, X. Zhang, C. Zhao and J. Yuan, *Mater. Chem. Front.*, 2023, **7**, 1423–1430.
- Z. Ding, S. Li, Y. Jiang, D. Wang and M. Yuan, *Nanoscale*, 2023, **15**, 3713–3729.
- M. Li, R. Begum, J. Fu, Q. Xu, T. M. Koh, S. A. Veldhuis, M. Graetzel, N. Mathews, S. Mhaisalkar and T. C. Sum, *Nat. Commun.*, 2018, **9**, 4197.
- Y. Deng, F. Peng, Y. Lu, X. Zhu, W. Jin, J. Qiu, J. Dong, Y. Hao, D. Di, Y. Gao, T. Sun, M. Zhang, F. Liu, L. Wang, L. Ying, F. Huang and Y. Jin, *Nat. Photonics*, 2022, **16**, 505–511.
- M. Xie, J. Guo, X. Zhang, C. Bi, X. Sun, H. Li, L. Zhang, D. Binks, G. Li, W. Zheng and J. Tian, *Adv. Funct. Mater.*, 2023, **33**, 2300116.
- Y.-K. Wang, F. Jia, X. Li, S. Teale, P. Xia, Y. Liu, P. T.-S. Chan, H. Wan, Y. Hassan, M. Imran, H. Chen, L. Grater, L.-D. Sun, G. C. Walker, S. Hoogland, Z.-H. Lu, C.-H. Yan, L.-S. Liao and E. H. Sargent, *Sci. Adv.*, 2023, **9**, eadh2140.
- Q. Zhao, A. Hazarika, X. Chen, S. P. Harvey, B. W. Larson, G. R. Teeter, J. Liu, T. Song, C. Xiao, L. Shaw, M. Zhang, G. Li, M. C. Beard and J. M. Luther, *Nat. Commun.*, 2019, **10**, 2842.
- L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692–3696.
- F. Zhang, H. Zhong, C. Chen, X.-G. Wu, X. Hu, H. Huang, J. Han, B. Zou and Y. Dong, *ACS Nano*, 2015, **9**, 4533–4542.
- X. Li, Y. Wu, S. Zhang, B. Cai, Y. Gu, J. Song and H. Zeng, *Adv. Funct. Mater.*, 2016, **26**, 2435–2445.
- K. N. Ganesh, D. Zhang, S. J. Miller, K. Rossen, P. J. Chirik, M. C. Kozlowski, J. B. Zimmerman, B. W. Brooks, P. E. Savage, D. T. Allen and A. M. Voutchkova-Kostal, *Environ. Sci. Technol.*, 2021, **55**, 8459–8463.
- H. C. Erythropel, J. B. Zimmerman, T. M. de Winter, L. Petitjean, F. Melnikov, C. H. Lam, A. W. Lounsbury, K. E. Mellor, N. Z. Jankovic, Q. Tu, L. N. Pincus, M. M. Falinski, W. Shi, P. Coish, D. L. Plata and P. T. Anastas, *Green Chem.*, 2018, **20**, 1929–1961.
- K. L. Gardner, J. G. Tait, T. Merckx, W. Qiu, U. W. Paetzold, L. Kootstra, M. Jaysankar, R. Gehlhaar, D. Cheyns, P. Heremans and J. Poortmans, *Adv. Energy Mater.*, 2016, **6**, 1600386.
- M. T. Hoang, F. Unlu, W. Martens, J. Bell, S. Mathur and H. Wang, *Green Chem.*, 2021, **23**, 5302–5336.
- D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2016, **18**, 288–296.
- F. Bisconti, A. Giuri, R. Suhonen, T. M. Kraft, M. Ylikunnari, V. Holappa, R. Po, P. Biagini, A. Savoini, G. Marra, S. Colella and A. Rizzo, *Cell Rep. Phys. Sci.*, 2021, **2**, 10063.
- D. Wang, J. Chen, P. Zhu, Y. Qiao, H. Hu, J. Zeng, J. Zhang, G. Qu, Y. Wang, X. Wang, A. K. Y. Jen and B. Xu, *Adv. Energy Mater.*, 2023, **13**, 2203649.
- N. Zhang, Z. Zhang, T. Liu, T. He, P. Liu, J. Li, F. Yang, G. Song, Z. Liu and M. Yuan, *Org. Electron.*, 2023, **113**, 106709.
- J. Li, X. Hua, F. Gao, X. Ren, C. Zhang, Y. Han, Y. Li, B. Shi and S. Liu, *J. Energy Chem.*, 2022, **66**, 1–8.
- R. Xia, Y. Xu, B. Chen, H. Kanda, M. Franckevicius, R. Gegevičius, S. Wang, Y. Chen, D. Chen, J. Ding, N. Yuan, Y. Zhao, C. Roldan-Carmona, X. Zhang, P. J. Dyson and M. K. Nazeeruddin, *J. Mater. Chem. A*, 2021, **9**, 21939–21947.
- X. Tang, Z. Wang, D. Wu, Z. Wu, Z. Ren, R. Li, P. Liu, G. Mei, J. Sun, J. Yu, F. Zheng, W. C. H. Choy, R. Chen, X. W. Sun, F. Yang and K. Wang, *Adv. Sci.*, 2022, **9**, 2104788.
- L. Zheng, K. Jiang, X. Li, P. Hong, K. Chen, H. Zhang, Y. Song and B. Luo, *J. Colloid Interface Sci.*, 2021, **598**, 166–171.
- Q. Zhang, F. Guo, R.-C. Zhao and Z.-H. Mo, *New J. Chem.*, 2023, **47**, 9771–9778.
- X. Liang, M. Chen, Q. Wang, S. Guo and H. Yang, *Angew. Chem., Int. Ed.*, 2019, **58**, 2799–2803.
- S. M. Jain, T. Edvinsson and J. R. Durrant, *Commun. Chem.*, 2019, **2**, 91.
- X. Wu, Y. Zheng, J. Liang, Z. Zhang, C. Tian, Z. Zhang, Y. Hu, A. Sun, C. Wang, J. Wang, Y. Huang, Z. Zhang, K. M. Reddy and C.-C. Chen, *Mater. Horiz.*, 2023, **10**, 122–135.
- C. Liu, L. Huang, X. Zhou, X. Wang, J. Yao, Z. Liu, S. F. Liu, W. Ma and B. Xu, *Sci. Bull.*, 2021, **66**, 1419–1428.
- X. Wang, Z. Han, F. Gao, C. Luo and Q. Zhao, *Solar RRL*, 2022, **6**, 2100973.
- T. Bu, L. Wu, X. Liu, X. Yang, P. Zhou, X. Yu, T. Qin, J. Shi, S. Wang, S. Li, Z. Ku, Y. Peng, F. Huang, Q. Meng, Y.-B. Cheng and J. Zhong, *Adv. Energy Mater.*, 2017, **7**, 1700576.
- Y. Kumar, O. Andres Jaramillo-Quintero, J. J. Jeronimo Rendon, T. Diaz Perez, M. E. Rincon and X. Mathew, *Sol. Energy*, 2019, **189**, 285–290.
- Y. Yun, F. Wang, H. Huang, Y. Fang, S. Liu, W. Huang, Z. Cheng, Y. Liu, Y. Cao, M. Gao, L. Zhu, L. Wang, T. Qin and W. Huang, *Adv. Mater.*, 2020, **32**, 1907123.
- Y. Miao, M. Ren, Y. Chen, H. Wang, H. Chen, X. Liu, T. Wang and Y. Zhao, *Nat. Sustainability*, 2023, **6**, 1–9, DOI: [10.1038/s41893-023-01196-4](#).
- X. Wu, Y. Zheng, J. Liang, Z. Zhang, C. Tian, Z. Zhang, Y. Hu, A. Sun, C. Wang, J. Wang, Y. Huang, Z. Zhang, K. M. Reddy and C.-C. Chen, *Mater. Horiz.*, 2023, **10**, 122–135.
- N.-G. Park, *Nat. Sustainability*, 2021, **4**, 192–193.
- H.-S. Yun, H. W. Kwon, M. J. Paik, S. Hong, J. Kim, E. Noh, J. Park, Y. Lee and S. I. Seok, *Nat. Energy*, 2022, **7**, 828–834.
- Z. Li, Q. Hu, Z. Tan, Y. Yang, M. Leng, X. Liu, C. Ge, G. Niu and J. Tang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 43915–43922.
- S. Ghosh and P. Kar, *ACS Appl. Electron. Mater.*, 2022, **4**, 2753–2759.
- A. Ito, K. Kamogawa, H. Sakai, K. Hamano, Y. Kondo, N. Yoshino and M. Abe, *Langmuir*, 1997, **13**, 2935–2942.
- C. Reichardt and T. Welton, *Solvents and solvent effects in organic chemistry*, John Wiley & Sons, 2011.



- 54 C. Geng, S. Xu, H. Zhong, A. L. Rogach and W. Bi, *Angew. Chem., Int. Ed.*, 2018, **57**, 9650–9654.
- 55 M. Aminzare, E. Hamzehpoor, S. Mahshid and N.-M. D. Courchesne, *ACS Appl. Nano Mater.*, 2022, **5**, 12666–12678.
- 56 X.-L. Wei, X.-D. Hu, L. Jiang, Q.-L. Shi and S.-W. Wu, *J. Nanopart. Res.*, 2023, **25**, 5.
- 57 X. Tang, X. Wen and F. Yang, *Nanoscale*, 2022, **14**, 17641–17653.
- 58 X. Tang, S. Weng, W. Hao and F. Yang, *ACS Sustainable Chem. Eng.*, 2023, **11**, 9121–9131.
- 59 N. Pradhan, D. Reifsnnyder, R. Xie, J. Aldana and X. Peng, *J. Am. Chem. Soc.*, 2007, **129**, 9500–9509.
- 60 Y. Yin and A. P. Alivisatos, *Nature*, 2005, **437**, 664–670.
- 61 Y. Zhang, T. D. Siegler, C. J. Thomas, M. K. Abney, T. Shah, A. De Gorostiza, R. M. Greene and B. A. Korgel, *Chem. Mater.*, 2020, **32**, 5410–5423.
- 62 S. E. Creutz, E. N. Crites, M. C. De Siena and D. R. Gamelin, *Nano Lett.*, 2018, **18**, 1118–1123.
- 63 X. Tang, N. L. Kothalawala, Y. Zhang, D. Qian, D. Y. Kim and F. Yang, *Chem. Eng. J.*, 2021, **425**, 131456.
- 64 X. Tang, Y. Zhang, N. L. Kothalawala, X. Wen, D. Y. Kim and F. Yang, *Nanotechnology*, 2022, **33**, 235605.
- 65 F. Yu, *Part. Sci. Technol.*, 2021, **39**, 91–100.
- 66 K. Umemoto, H. Ebe, R. Sato, J. Enomoto, N. Oshita, T. Kimura, T. Inose, T. Nakamura, T. Chiba, S. Asakura, H. Uji-I and A. Masuhara, *ACS Sustainable Chem. Eng.*, 2020, **8**, 16469–16476.
- 67 M. Liu, Q. Wan, H. Wang, F. Carulli, X. Sun, W. Zheng, L. Kong, Q. Zhang, C. Zhang, Q. Zhang, S. Brovelli and L. Li, *Nat. Photonics*, 2021, **15**, 379–385.
- 68 Q. Chen, J. Wu, X. Ou, B. Huang, J. Almutlaq, A. A. Zhumekenov, X. Guan, S. Han, L. Liang, Z. Yi, J. Li, X. Xie, Y. Wang, Y. Li, D. Fan, D. B. L. Teh, A. H. All, O. F. Mohammed, O. M. Bakr, T. Wu, M. Bettinelli, H. Yang, W. Huang and X. Liu, *Nature*, 2018, **561**, 88–93.
- 69 M. Biliroglu, G. Findik, J. Mendes, D. Seyitliyev, L. Lei, Q. Dong, Y. Mehta, V. V. Temnov, F. So and K. Gundogdu, *Nat. Photonics*, 2022, **16**, 324–329.
- 70 Z. Long, H. Ren, J. Sun, J. Ouyang and N. Na, *Chem. Commun.*, 2017, **53**, 9914–9917.
- 71 Y. Li, H. Huang, Y. Xiong, S. V. Kershaw and A. L. Rogach, *Angew. Chem., Int. Ed.*, 2018, **57**, 5833–5837.
- 72 J. De Roo, M. Ibanez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I. Van Driessche, M. V. Kovalenko and Z. Hens, *ACS Nano*, 2016, **10**, 2071–2081.
- 73 R. Grisorio, M. E. Di Clemente, E. Fanizza, I. Allegretta, D. Altamura, M. Striccoli, R. Terzano, C. Giannini, M. Irimia-Vladu and G. P. Suranna, *Nanoscale*, 2019, **11**, 986–999.
- 74 Q. A. Akkerman, T. P. T. Nguyen, S. C. Boehme, F. Montanarella, D. N. Dirin, P. Wechsler, F. Beiglbock, G. Raino, R. Erni, C. Katan, J. Even and M. V. Kovalenko, *Science*, 2022, **377**, 1406–1412.
- 75 F. P. G. de Arquer, D. V. Talapin, V. I. Klimov, Y. Arakawa, M. Bayer and E. H. Sargent, *Science*, 2021, **373**, eaaz8541.
- 76 G. H. Carey, A. L. Abdelhady, Z. Ning, S. M. Thon, O. M. Bakr and E. H. Sargent, *Chem. Rev.*, 2015, **115**, 12732–12763.
- 77 H. Xiao, Y. Wei, P. Dang, S. Liang, Z. Cheng, G. Li and J. Lin, *J. Mater. Chem. C*, 2020, **8**, 9968–9974.
- 78 F. Yang, *Phys. Lett. A*, 2022, **428**, 127931.
- 79 Z. Tan, J. Li, C. Zhang, Z. Li, Q. Hu, Z. Xiao, T. Kamiya, H. Hosono, G. Niu, E. Lifshitz, Y. Cheng and J. Tang, *Adv. Funct. Mater.*, 2018, **28**, 1801131.
- 80 Q. Chen, X. Yang, Y. Zhou and B. Song, *New J. Chem.*, 2021, **45**, 15118–15130.
- 81 Y. Xia, C. Zhao, P. Zhao, L. Mao, Y. Ding, D. Hong, Y. Tian, W. Yan and Z. Jin, *J. Power Sources*, 2021, **494**, 229781.
- 82 M. A. Haque, D. R. Villalva, L. H. Hernandez, R. Tounesi, S. Jang and D. Baran, *Chem. Mater.*, 2021, **33**, 8147–8172.
- 83 M. Zhu, Y. Xia, L. Qin, K. Zhang, J. Liang, C. Zhao, D. Hong, M. Jiang, X. Song, J. Wei, P. Zhang, Y. Tian and Z. Jin, *Nano Res.*, 2023, **16**, 6849–6858.
- 84 B. Xue, L. Wang and Y. Li, *J. Phys. Chem. Lett.*, 2022, **13**, 1180–1186.
- 85 Y. Xia, M. Zhu, L. Qin, C. Zhao, D. Hong, Y. Tian, W. Yan and Z. Jin, *Energy Mater.*, 2023, **3**, 300004.
- 86 Y. Gao, C. Yan, X. Peng, W. Li, J. Cao, Q. Wang, X. Zeng, X. Fu and W. Yang, *Nanoscale*, 2021, **13**, 18010–18031.
- 87 M. Zhu, L. Qin, Y. Xia, L. Mao, P. Zhao, C. Zhao, Y. Hu, D. Hong, Y. Tian, Z. Tie and Z. Jin, *ACS Appl. Energy Mater.*, 2023, **6**, 8237–8244.
- 88 S. Zhou, Y. Ma, G. Zhou, X. Xu, M. Qin, Y. Li, Y.-J. Hsu, H. Hu, G. Li, N. Zhao, J. Xu and X. Lu, *ACS Energy Lett.*, 2019, **4**, 534–541.
- 89 M. Zhu, L. Qin, Y. Xia, J. Liang, Y. Wang, D. Hong, Y. Tian, Z. Tie and Z. Jin, *Nano Res.*, 2023, DOI: [10.1007/s12274-023-5981-7](https://doi.org/10.1007/s12274-023-5981-7).
- 90 P. K. Nayak, M. Sendner, B. Wenger, Z. Wang, K. Sharma, A. J. Ramadan, R. Lovrincic, A. Pucci, P. K. Madhu and H. J. Snaith, *J. Am. Chem. Soc.*, 2018, **140**, 574–577.
- 91 M. Zhu, L. Qin, Y. Xia, Y. Hu, X. Song, D. Hong, Y. Tian, Z. Tie and Z. Jin, *Sustainable Energy Fuels*, 2023, **7**, 4127–4135.
- 92 S. Lou, Z. Zhou, W. Gan, T. Xuan, Z. Bao, S. Si, L. Cao, H. Li, Z. Xia and J. Qiu, *Green Chem.*, 2020, **22**, 5257–5261.
- 93 M. Chen, X. Zhang, C. Luo, R. Qi, H. Peng and H. Lin, *ACS Appl. Mater. Interfaces*, 2021, **13**, 20622–20632.
- 94 Q. Wang, B. Chen, Y. Liu, Y. Deng, Y. Bai, Q. Dong and J. Huang, *Energy Environ. Sci.*, 2017, **10**, 516–522.
- 95 A. Mei, Y. Sheng, Y. Ming, Y. Hu, Y. Rong, W. Zhang, S. Luo, G. Na, C. Tian, X. Hou, Y. Xiong, Z. Zhang, S. Liu, S. Uchida, T.-W. Kim, Y. Yuan, L. Zhang, Y. Zhou and H. Han, *Joule*, 2020, **4**, 2646–2660.
- 96 Y. Wei, X. Deng, Z. Xie, X. Cai, S. Liang, P. A. Ma, Z. Hou, Z. Cheng and J. Lin, *Adv. Funct. Mater.*, 2017, **27**, 1703535.
- 97 H. Zhang, X. Wang, Q. Liao, Z. Xu, H. Li, L. Zheng and H. Fu, *Adv. Funct. Mater.*, 2017, **27**, 1604382.
- 98 Z.-J. Li, E. Hofman, J. Li, A. H. Davis, C.-H. Tung, L.-Z. Wu and W. Zheng, *Adv. Funct. Mater.*, 2018, **28**, 1704288.
- 99 Q. Zhong, M. Cao, H. Hu, D. Yang, M. Chen, P. Li, L. Wu and Q. Zhang, *ACS Nano*, 2018, **12**, 8579–8587.
- 100 X. Tang, J. Yang, S. Li, Z. Liu, Z. Hu, J. Hao, J. Du, Y. Leng, H. Qin and X. Lin, *Adv. Sci.*, 2019, **6**, 1900412.
- 101 V. K. Ravi, S. Saikia, S. Yadav, V. V. Nawale and A. Nag, *ACS Energy Lett.*, 2020, **5**, 1794–1796.