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Uniform growth of perovskite nanocrystals

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Monodisperse perovskite nanocrystals are formed by using a diffusion-mediated growth mechanism that controls converted monomer concentration such that premature termination or secondary growth processes are prevented.

Organic–inorganic hybrid perovskite nanocrystals (PNCs) with size control beyond conventional quantum dots[1] have garnered interest owing to their vivid colours and tunable optical properties. As a result, PNCs have been used in optoelectronic devices, such as light-emitting diodes (LEDs)[2–5] and solar cells[6–9]. However, making uniform and monodisperse hybrid PNCs has long been a challenge. The primary issue lies in the rapid and uncontrollable reaction kinetics as a consequence of their ionic nature and low lattice formation energy[10,11]. In traditional methods, such as the hot injection or ligand-assisted reprecipitation methods, the reaction between organic cations and lead halide precursors occurs almost instantaneously, often leading to uncontrolled nucleation and rapid growth. This lack of control over reaction kinetics results in broad size distributions of the nanocrystals that cause size defocusing, and the short reaction time to avoid Ostwald ripening also causes size defocusing.

Now, writing in *Nature Synthesis*, Sun, Liu, Ma and co-workers report a diffusion-mediated synthesis method that mitigates the challenges of rapid kinetics and uncontrolled supply of precursors (Fig. 1)[12]. In conventional synthetic approaches, binary precursors[13] such as formamidinium oleate (FA-oleate) and lead halide (PbX_2) or ternary precursors[14] like FA-oleate, lead oleate (Pb-oleate), and oleylammonium halide are commonly used. A problem in these traditional methods is the excess availability of soluble precursors, which leads to rapid nucleation and growth simultaneously, resulting in the formation of PNC with a broad size distribution.

The diffusion-mediated synthesis introduces a slower, more controlled growth mechanism. This growth is achieved by using lead thiocyanate ($Pb(SCN)_2$) as a Pb source, which has limited solubility owing to robust binding affinity between Pb and thiocyanate ions. Unlike more commonly used Pb sources such as PbX_2 or Pb-oleate, $Pb(SCN)_2$ partially dissolves, initially providing a limited amount of monomer and releasing more as the reaction consumes the converted monomer. This steady supply helps maintain a relatively high monomer concentration, allowing the system to remain in the size-focusing regime for an extended period – up to 180 minutes – enabling uniform PNC growth and preventing premature termination or secondary growth processes.

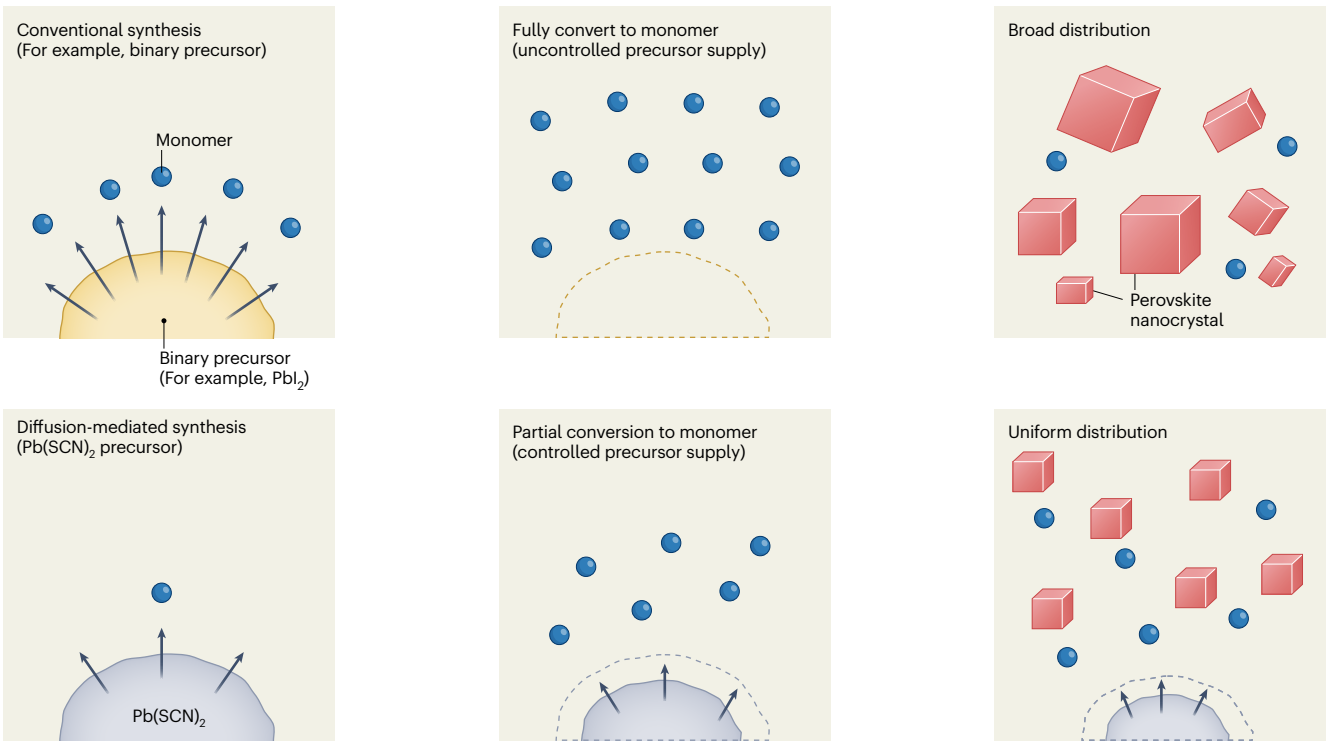

Fig. 1 | Formation pathways for perovskite nanocrystals (PNCs). Schematic representation comparing the conventional synthesis, where rapid monomer depletion leads to size-defocusing, and the diffusion-mediated synthesis, where controlled monomer release ensures size-focused growth and prevents Ostwald ripening.

Additionally, the presence of bulk and solid-phase $Pb(SCN)_2$ reduces the mass transfer of monomers from the solution to the nanocrystal surfaces, facilitating a diffusion-controlled model. When two different sizes of PNCs that were produced at different reaction times are mixed, the smaller PNCs grow faster than the larger ones, indicating that PNC growth using $Pb(SCN)_2$ follows a diffusion-mediated growth model, which is advantageous for the formation of monodispersed PNCs.

The diffusion-mediated approach produces monodisperse hybrid PNCs and can be extended to the synthesis of various hybrid perovskites. Uniform PNCs with the maximum and minimum diameters within 1 nm of the average were formed in all $FAPbX_3$ and $MAPbX_3$ (X = I, Br, Cl) systems, exhibiting the optical properties of uniform PNCs. Compared to control $FAPbI_3$ PNCs synthesized via the ternary-precursor method, the diffusion-mediated $FAPbI_3$ PNCs show a narrower full width at half maximum (FWHM) in both transient absorption spectra (50.0 nm compared with 63.3 nm) and time-resolved photoluminescence spectra (42.5 nm compared with 60.2 nm). Additionally, the diffusion-mediated PNCs show a substantially longer average transient absorption lifetime (868 ps compared with 328 ps) and photoluminescence lifetime (10.9 ns compared with 4.3 ns), indicating slower energy transfer due to improved uniformity.

Moreover, in the diffusion-mediated approach, $Pb(SCN)_2$ not only facilitates uniform growth but also suppresses defect formation through SCN ions, contributing to the successful achievement of near-unity photoluminescence quantum yield (PLQY) in red- and green-emitting hybrid PNCs. Specifically, $FAPbX_3$ PNCs reached near-unity PLQY, and $MAPbX_3$ PNCs achieved a PLQY of over 94%, demonstrating the versatility of the diffusion-mediated approach in monodispersity and defect suppression. Sun, Liu, Ma and co-workers proceed to fabricate a high-efficiency solar cell with a power conversion efficiency (PCE) of 16.66% using these monodispersed, high-PLQY PNCs.

The diffusion-controlled growth process offers exciting possibilities for further exploration. The high uniformity of PNCs ensures consistent optoelectronic properties, particularly in applications where precise emission wavelengths are required, such as in optical communications and single-photon emitters. Monodispersed nanocrystals are critical for minimizing performance variability in these applications, as even small variations in size of PNCs below exciton Bohr diameter can lead to substantial shifts in emission wavelength and efficiency. This level of size control also enhances the optical coherence and stability of devices, making them ideal for optoelectronic devices.

Additionally, the diffusion-mediated approach enables the investigation of fundamental questions about the nucleation and growth of PNCs. With greater control over the kinetics, researchers can now explore how different precursor combinations, ligand types, and growth conditions affect the crystal structure and surface chemistry of hybrid PNCs. This information may lead to the development of more controlled or complex nanostructures, such as core–shell architectures or doped systems, which could improve their stability and performance in applications. Overall, this work is an advance in the synthesis of organic–inorganic hybrid PNCs, offering a robust method for producing uniform and high-performance PNCs, which could enhance the development of next-generation optoelectronic devices and energy technologies.

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Competing interests

The authors declare no competing interests.