

# The real dope: Improving perovskite nanomaterials in flow

Julia Nette<sup>1</sup> and Andrew J. deMello<sup>1,\*</sup>

**Microfluidic tools have shown significant utility in the synthesis of high-quality nanomaterials. In this issue of *Matter*, Bateni et al. showcase an automated, modular microfluidic platform with *in situ* optical characterization using post-synthetic manganese doping of CsPbCl<sub>3</sub> Quantum Dots.**

In the world of light-emitting nanomaterials, all inorganic metal halide perovskite quantum dots (PQDs) are notable for their outstanding optical properties and the ease by which they can be synthesized and subsequently modified. Unsurprisingly, such features make them ideal for a range of contemporary photovoltaic and light-emitting applications, with PQDs already having some impact in next-generation solar cells.<sup>1</sup> Despite their undoubted popularity, PQD implementation within commercial devices is still far from routine, primarily due to the high perceived toxicity of lead and the unacceptably low operational stabilities of PQD-based devices. Because substitutes for lead are subject to both size and electronic requirements to maintain structural integrity and optical properties, the journey to high-performance lead-free perovskites is a rocky one. In this regard, an alternative and highly promising route to minimizing lead content in PQDs while enhancing optical properties involves the partial exchange of lead ions with less toxic materials having appropriate optoelectronic properties. Such an approach was first demonstrated by van der Stam and colleagues with the partial cation exchange of Pb<sup>2+</sup> for multiple isovalent ions in colloidal CsPbBr<sub>3</sub>, yielding doped CsPb<sub>1-x</sub>M<sub>x</sub>Br<sub>3</sub> nanocrystals, where M = Sn<sup>2+</sup>, Cd<sup>2+</sup>, and Zn<sup>2+</sup> and 0 < x ≤ 0.1.<sup>2</sup> More recently, Gao and coworkers reported partial and reversible cation exchange of

Pb<sup>2+</sup> and Mn<sup>2+</sup> in CsPbCl<sub>3</sub> nanocrystals to yield CsPb<sub>1-x</sub>Mn<sub>x</sub>Cl<sub>3</sub> nanocrystals with controllable photoluminescence.<sup>3</sup> Interestingly, Hills-Kimball and colleagues have also presented a cation exchange strategy for CsPbCl<sub>3</sub> nanocrystals, where Pb<sup>2+</sup> is partially replaced by Mn<sup>2+</sup> cations using a solid Mn<sup>2+</sup> precursor source under ambient conditions.<sup>4</sup>

Despite being ubiquitous, flask-based approaches for synthesizing and modifying nanomaterials suffer from multiple drawbacks, including batch-to-batch variability, poor control of mass and heat transfer and difficulties associated with real-time product analysis. Conversely, microfluidic systems are adept in transferring mass and energy in a rapid manner, allowing the creation or homogenization of temperature and reagent gradients on ultra-short time-scales. These features combined with the ability to sequentially add and remove reagents in a controlled manner and the simple integration of optical detection tools, have enabled the direct production of bespoke nanomaterials of variable and complex composition, as well as facile and rapid screening of parameters.<sup>5</sup> Unsurprisingly, since the first report of nanoparticle synthesis using a continuous flow microfluidic system in 2002,<sup>6</sup> countless microfluidic strategies have been used to excellent effect in the synthesis of variety of organic, inorganic, polymer,

noble metal and metal oxide nanoparticles having outstanding physical and chemical properties.

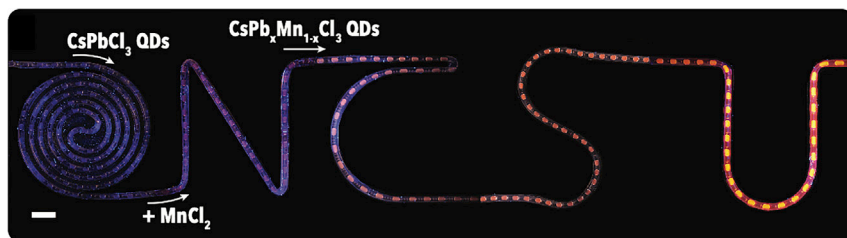
In this issue of *Matter*, Bateni et al.<sup>7</sup> elegantly extend the utility of microfluidic tools in the manufacturing of bespoke nanomaterials, presenting a microfluidic strategy for ultra-fast post-synthetic doping of cesium lead chloride perovskite quantum dots (Figure 1). At the heart of their discovery platform is a segmented flow microfluidic reactor, which allows the controllable addition and processing of CsPbCl<sub>3</sub> quantum dots and a MnCl<sub>2</sub> dopant stream. Such an arrangement enables surface doping through vacancy assisted cation migration, where lead cations are initially exchanged with manganese cations and then diffuse inward, preserving the structural integrity of the quantum dots. Importantly, when combined and integrated with multimodal product characterization (through UV-visible absorption and fluorescence spectroscopies), the system allows for a thorough and accelerated study of a material within the temporal, temperature and pressure limits of the system.

This sophisticated microfluidic platform is surprisingly simple in construction and outshines classical flask-based approaches for the post-synthetic modification of metal cation-doped PQDs in almost all aspects. Reactions are performed in an automated fashion, and because product characterization occurs instantaneously, the optical and electronic properties of the metal cation-doped PQDs can be precisely controlled and optimized, with doping efficiency being quantified through emission characteristics and structural

<sup>1</sup>Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland

\*Correspondence:  
[andrew.demello@chem.ethz.ch](mailto:andrew.demello@chem.ethz.ch)  
<https://doi.org/10.1016/j.matt.2021.06.017>





**Figure 1. Facile cation doping of CsPbCl<sub>3</sub> QDs in flow**

Precise tuning of the metal cation doping of CsPbCl<sub>3</sub> QDs in flow under UV irradiation (365 nm). Scale bar, 9 mm. Reprinted from Bateni et al.<sup>7</sup>

properties (such as size and stability) being accessed via absorption measurements. Although similar systems for nanomaterial synthesis have been previously reported, the current system is notable regarding its ability to extract kinetic information regarding the manganese-doping process in a robust manner. As with all flow-based reactors, the correspondence between reaction time and distance along the flow path allows kinetic measurements to be made in a direct manner. That said, the clever addition of an inert gas phase to the standard two-phase (liquid-liquid) flow is used to establish a three-phase flow, which engenders additional and significant improvements in flow control, reagent mixing, and time resolution. Such a flow regime is especially useful in the current case, as cation doping processes are almost always extremely fast.

Specifically, the team's post-synthetic doping approach involves mixing a manganese dopant flow (manganese chloride in octadecene-oleylamine) with a flow of purified CsPbCl<sub>3</sub> quantum dots at T-junction. Upon purification, PQDs develop chloride vacancies and structural distortions, which unsurprisingly have a strong influence on the optical characteristics of the particles. When added, the dopant system can both replace lead ions and additionally fill chloride vacancies, which aids structural integrity while also improving their emission properties. In this regard, the nature of the manganese precursor is noteworthy, since it comprises an

MnCl<sub>2</sub>-oleylamine complex, free chloride ions and oleylammonium ions, with the oleylammonium ions binding to halide sites at the particle surface, free chloride ions filling halide vacancies and MnCl<sub>2</sub> octahedra replacing PbCl<sub>2</sub> octahedra.<sup>3,8</sup>

The authors use their platform to systematically assess the effects of dopant concentration and ligand composition (ligand-to-solvent ratio) on the efficiency and kinetics of the doping process and show that although the extent of doping initially increases with increasing Mn<sup>2+</sup> concentration, for MnCl<sub>2</sub> concentrations above 18 mM, doping decreases due to an increased number of inactivated Mn<sup>2+</sup> ions in solution, which prevent MnCl<sub>2</sub>-octahedra from reaching the particle surface. Similarly, an increase in the ligand-to-solvent ratio initially improves the doping process, but deteriorates particles once the ligand-to-solvent ratio exceeds 0.1. Based on these observations, and the ability to perform measurements on a millisecond timescale, the authors propose a two-step mechanism describing post-synthetic manganese-doping of CsPbCl<sub>3</sub> quantum dots. First, within the initial 500 ms of reaction, defects in the quantum dots are removed, with the surface being ligand enriched and stabilized. At later times, this is followed by cation exchange between lead and manganese ions. Importantly, cation exchange occurs via the surface, with the dopant never fully reaching the particle core, thus guaranteeing structure conserva-

tion. Since manganese-doped regions are characterized by red-shifted photoluminescence, the extent of doping is easily observable via the emission profile.

To conclude, the presented microfluidic platform elegantly leverages a space-to-time strategy to elucidate the fundamental mechanism controlling the doping of CsPbCl<sub>3</sub> quantum dots with manganese cations, and further allows for exquisite control over the resulting optoelectronic properties, paving the way for the scalable synthesis of bespoke metal cation-doped PQDs. In this regard, the autonomous nature of this robotic platform cannot be overstated, with the integration of *in situ* product characterization granting insights into reactive processes that would only in principle be accessible to flask-based approaches after weeks of continuous experimentation. Indeed, such features highlight the ease with which a range of novel optoelectronic materials may be generated and subsequently refined, with complete mechanistic and formulation studies being possible over short timescales and with minimal reagent consumption.

Aside from the timely application of this automated microfluidic platform to ultra-fast post-synthetic doping of cesium lead chloride perovskite quantum dots, the presented platform and the underlying control architecture represent a significant new tool for bespoke material development and discovery. Indeed, it will be interesting to see how easy it will be to extend the upstream microfluidic workflow to include modules for the synthesis of metal halide and mixed halide perovskite quantum dots prior to particle doping. Such a system would undoubtedly offer significant opportunities for generating new and unique formulations inaccessible to conventional synthetic methods. Finally, the environmental credentials of the platform are compelling, with low overall material

consumption and the ability to drastically reduce PQD lead content. Put simply, automated microfluidic platforms of the kind presented by Bateni and co-workers open up a plethora of new opportunities for the synthesis, discovery and modification of new optoelectronic materials and material formulations.<sup>9</sup> Although there is still much to do, it is fair to say that microfluidic tools are becoming indispensable in nanomaterials research and development.

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## Bioinspired stiff yet tough healable nanocomposites: From molecular design to structural processing

Min Gong<sup>1,2</sup> and Pengbo Wan<sup>1,\*</sup>

**A stiff yet tough healable nanocomposite assembled from supramolecular polymer and MXene nanosheets was reported through molecular design and structural processing, offering an inspiring strategy of richly designed soft polymers in a rigid inorganic framework to integrate desirable attributes.**

The prospering flexible and wearable electronics are poised to revolutionize the future lifestyles of human beings for their tremendous virtues of softness, lightweight, transparency, and portability.<sup>1</sup> To extend the lifetime and reduce maintenance costs of the devices, mechanically robust and healable materials, capable of autonomously repairing physical damage, are highly demanded. In this respect, the predominant strategies for obtaining intrinsic self-healing capability are molecularly programming noncovalent

bonds or reversible (dynamic) covalent bonds as healing motifs.<sup>2</sup> Particularly, supramolecular chemistry—which is based on the non-covalent bonding including hydrogen bonding, metal-ligand coordination,  $\pi$ - $\pi$ , ionic, guest-host, and van der Waals interactions—has attracted extensive research interest and driven considerable crosslinked assemblies. The chain mobility of the supramolecular can be significantly enhanced under the corresponding external stimulus by disassociating the in-

teractions, leading to stimuli-responsive healing behaviors.<sup>3</sup> However, the contradictory requirements for molecular structures lead to the trade-off between the mechanical properties (robustness and toughness) and the self-healing performance. Typically, a large number of non-covalent interactions may lead to better mechanical strength, but the fracture toughness of materials would be inevitably compromised, resulting in the rigid and brittle nature as well as the catastrophic failure during long-term usage.

Concerning increased strength and toughness, considerable progress has

<sup>1</sup>Interdisciplinary Research Center for Artificial Intelligence, College of Materials Science and Engineering, State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

<sup>2</sup>School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China

\*Correspondence: [pbwan@mail.buct.edu.cn](mailto:pbwan@mail.buct.edu.cn)  
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