



Research Highlight

Halide perovskite nanocrystals can also stand luminescent in water

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Perovskite nanocrystals (PNCs) are merging as a rising star in the field of optoelectronic materials [1]. Apart from the great potentials in display, photovoltaics and optical sensors, etc. [2], they may become an alternative choice of conventional cadmium chalcogenides, e.g., CdSe and CdTe quantum dots (QDs), for biological and biomedical applications. Nevertheless, the extremely moisture-sensitive nature of halide perovskites set a huge hurdle towards the latter applications as well as other possible applications in humid environments [3].

Aqueous solubility or dispersity is essentially required for the bio-applications of luminescent nanoparticles, irrespective of particle types including fluorescent QDs, upconversion nanoparticles (NPs), and PNCs [4]. In general, there are two general ways to achieve the aqueous solubility or dispersity for luminescent nanoparticles. The first one is to transfer the preformed hydrophobic nanocrystals from non-polar system into aqueous system through either ligand exchange or surface over-coating with an amphiphilic ligand or silica, while the second one is to directly synthesize the luminescent nanoparticles in aqueous systems. Since water is a strong polar solvent that can induce surface dynamics leading to surface defects for photo-generated carriers, the luminescence is often largely quenched when the hydrophobic luminescent particles are transferred into aqueous systems no matter which of the aforementioned methods is adopted. Due to the extremely low solubility products, QDs and rare-earth based nanoparticles can at least survive in aqueous systems, although a big percentage of luminescence is gone in many cases. In huge contrast, the halide perovskites are water soluble, to disperse PNCs in water thus becomes extremely challenging [5–7].

Very recently, Chinese researchers have achieved remarkable progress in obtaining luminescent PNCs in aqueous systems [8,9]. The first successful approach is based on effective isolation of PNCs from environmental water, enabled by a hydrophobic corona introduced around the PNCs. In collaboration with Prof. Haizheng Zhong from Beijing Institute of Technology (BIT), Prof. Kun Liu's group at Jilin University designed an amphiphilic block polymer for transferring the PNCs formed in non-polar system into aqueous system. They found that the real challenge is how to form a protective hydrophobic corona on surface of PNCs with the hydrophobic segment of a block co-polymer. In their study, an amine-terminated polystyrene-*b*-poly(ethyl oxide) ($\text{H}_2\text{N-PS-}b\text{-PEO}$) ligand was

synthesized and used instead of oleylamine to yield MAPbBr_3 (MA = methylammonium) NCs of 3.3 nm in toluene. Although the PS-*b*-PEO seems to be a perfect ligand for transferring the underlying NCs into aqueous system, a fast degradation of PNCs was observed after water was introduced into the non-polar solution of the PNCs. To solve this problem, the authors proposed a very smart “detour strategy” by packing the polymer ligands prior to the phase transferring process. In detail, they precipitated the polymer-coated PNCs with hexane that is a bad solvent for both PS and PEO blocks. In this way, a micro-phase separation between PS and PEO blocks is induced to form a densely-packed polystyrene corona around the PNC cores. In consequence, the resulting PNCs become well dispersible in water and exhibit strong photoluminescence with a quantum yield up to 43% at room temperature, high colour purity with the full width at half maxima close to 18 nm, and long average photoluminescence lifetimes up to 164 ns. In addition, the aqueous colloidal PNCs also show excellent thermo- and photostability, low cytotoxicity, and good resistance to the variation of pH in a broad range, which hopefully opens a wide door towards the bio-labelling applications of the PNCs.

In another work, Prof. Shu Xu and his colleagues at Hebei University of Technology also challenged the incompatibility between perovskite and water, and proposed a very straightforward synthetic approach (Fig. 1) [9]. In collaboration with Prof. Haizheng Zhong from BIT apart from Prof. Andrey Rogach from City University of Hongkong, they demonstrated that the PNCs can directly be stabilized by properly balancing the solubility equilibrium of $[\text{PbX}_6]^{4-}$ ($\text{X} = \text{halogen}$) and the protonation of methylamine in aqueous solution [9]. In principle, the formation of PbX_2 or $\text{Pb}(\text{OH})_2$ drives the decomposition of PNCs in aqueous system. Therefore, excessive halogen ions help slow down the decomposition of PNCs in aqueous systems. On the other hand, low pH promotes the protonation of methylamine, which remarkably pushes the reaction between methylamine and $[\text{PbX}_6]^{4-}$ to form methylammonium lead halide perovskite. Following these principles, the above researchers successfully obtained highly luminescent PNCs in a simple but very brilliant way, by properly balancing all reactions involved with halogenic acid [9]. They further unveiled that pH of the reaction system plays a critical role in obtaining PNCs colloiddally stabilized through the electrostatic repulsions. In addition, the PL quantum yield and photochemical stability of the PNCs can further be improved with surface capping agents, e.g., phenylalanine. This study may fundamentally change

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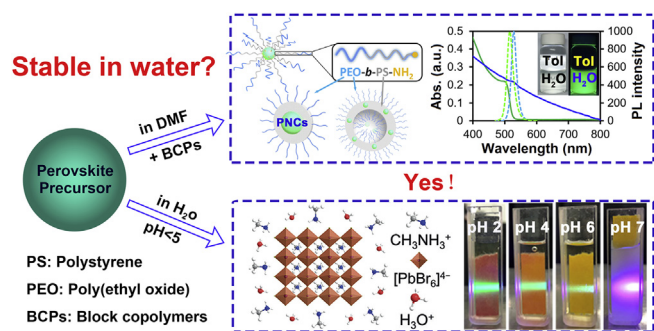


Fig. 1. (Color online) The strategies for obtaining aqueous colloidal perovskite nanocrystals.

the basic understanding of the aqueous stability of perovskites, and thus benefits the “green and sustainable” chemistry for perovskite nanocrystals with defined size, shape, and chemical compositions, which are waited by broad applications.

Conflict of interest

The author declares that he has no conflict of interest.

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