Lead halide perovskites: Recombining faster, emitting brighter

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Exciton is an electron-hole pair with Coulomb interaction, which represents the binding energy of the two particles. The electron and hole in exciton may have either the opposite or the parallel spin directions, corresponding to bright (emissive) singlet exciton or dark (non-emissive) triplet exciton, respectively. Triplet states lie below but are three times abundant than singlet states. It has been well established [1] that luminescence in semiconductor nanocrystals comes from the radiative recombination of bright singlet exciton. In a letter recently published in *Nature* [2], however, Becker and co-workers pointed out that in lead halide perovskites, a class of rapidly developing materials in both photovoltaic and light-emitting fields, the triplet exciton is highly emissive. It means a breakthrough in semiconductor optics, and could have strong implications for high brightness light-emitting diodes (LEDs).

Radiative lifetime is one of the key factors describing and determining the light-emitting properties of semiconductors. This can be understood mainly in two aspects: 1) the photoluminescence (PL) intensity (I_{PL}) is proportional to the radiative recombination rate (B) as $I_{\text{PL}} \sim Bn$, where n is the concentration of excitons in excited states. The recombination rate B is in inverse proportion to the radiative lifetime, namely, the shorter the lifetime, the higher the rate. 2) There are various nonradiative recombination or trapping channels in semiconductor materials, which are generally fast processes. Short radiative lifetime reduces the possibility of excitons being captured by such defect centers, thus enhancing the PL quantum yield (QY). In these regards, short radiative lifetime is essential to obtain high brightness of light-emitting materials and devices.

Unfortunately, the radiative recombination of excitons in most semiconductor nanocrystals is slow, with radiative lifetime in the sub-microsecond regime [3]. This re-

Figure 1 Three-level diagram for demonstrating the transitions between the excited and ground state of excitons in semiconductor nanocrystals at low temperature. (a) In general, the low-lying triplet state is dark. Luminescence from bright singlet state is delayed by thermalization process of triplet state to singlet state. (b) In CsPbBr₃ nanocrystal, the low-lying triplet state is bright while the singlet is dark. The transition from triplet to ground state is thus characterized by very short radiative lifetime.

sults from the presence of triplet excitons, which emit very slowly. As shown in Fig. 1, in semiconductor nanocrystals the dark triplet state of excitons is generally lower than the bright singlet state within several millielectronvolts (meV). The luminescence is thus delayed by the thermalization of the lower-lying occupied dark states to the bright singlet state. Such scenario has been well accepted for a long time. Surprisingly, Becker and co-workers [2] pointed out that in cesium lead halide perovskites this is not the case. By combining theoretical calculation with PL experiments at the single-nanocrystal level, they found that in CsPbBr₃ nanocrystals the lowest triplet exciton state is not dark but highly emissive. As a result, the luminescence no longer suffers from any delay demonstrated in Fig. 1, and shows very short radiative lifetime down to the sub-nanosecond regime, which is up to 1000 times faster than any other semiconductor nanocrystal.

It should be noted that in hybrid perovskite films the

bimolecular recombination rate of free carriers is rather low [4,5], which has been regarded as advantages to perovskite solar cells because it leads to very long carrier diffusion length. For light-emitting applications, excitonic emission and devices are desired [5]. However, the exciton binding energies of bulk perovskites are lower than or comparable to thermal energy [6], too low to support dominant excitonic emission at room temperature. The enhancement of excitonic emission can be realized by localization [7] or quantum confinement of excitons. In particular, exciton confined in various dimensions, such as nanocrystals and nanoplatelets, shows greatly enhanced exciton binding energy and oscillator strength [8], which are fundamental parameters determining the luminescence efficiency. Moreover, the very fast radiative recombination of excitons in CsPbBr₃ nanocrystals reported in Ref. [2] adds weight to the excellent properties of these materials for light-emitting applications, including very high PLQY, tunable wavelength in a broad spectral range, and wide color gamut.

The energy splitting between the triplet and singlet states in CsPbBr₃ nanocrystals is about 1 meV, which is much smaller than the thermal energy. At room temperature, these states are equally occupied and thus the role of triplet excitons in the room temperature PL efficiency remains to be clarified. Nevertheless, the finding of bright triplet excitons is of fundamental relevance and may have significant implication in searching and designing efficient light-emitting materials. For example, if the energy splitting between the dark triplet and bright singlet states is large enough to suppress the thermalization process, the internal quantum efficiency of PL will be limited to a low level, as widely known in organic semiconductors. The work of Becker and co-workers also points out the way to search more semiconductors with bright triplet states.

In recent years, rapid progress has been made in perovskite LEDs using either solution-processed thin films or colloidal nanocrystals [9]. External quantum efficiency

>10% [10,11] and ultrahigh brightness up to $5.9 \times 10^5 \text{ cd m}^{-2}$ [12] have been reported. The work of Becker *et al.* reinforces the idea that lead halide perovskites are excellent light emitters. We shall believe that there is a great future for perovskites in light-emitting as well as other optoelectronic devices.

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