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Research Highlight

Continuous-wave lasing from quasi-2D perovskites

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Miniaturized lasers at the micro- and nanoscale are highly attractive for applications in sensing, lighting, display, and highly-integrated photonic devices because of their advantages of low noise and good spectral purity [1–3]. Since the first demonstration of amplified spontaneous emission (ASE) behavior in solution-based $CH_3NH_3PbX_3$ perovskite film in 2014 [4], both pulsed and continuous-wave (CW) lasing have been realized in various metal halide perovskites due to their superior attributes [5,6]. Despite their better stability and higher exciton binding energy [7], CW lasing from quasi-two-dimensional (2D) perovskites has not been achieved because of the "lasing death" phenomenon (the sudden termination of lasing under constant operation). The mechanism leading to the lasing death phenomenon is still unclear, although some researchers have ascribed it to auger recombination loss, thermal runaway, or photoinduced structural change [8–10].

Recently, published in *Nature*, Qin et al. [11] indicate that the singlet–triplet exciton annihilation (STA) caused by the accumulation of long-lived triplet excitons may account for lasing death in quasi-2D perovskites. By managing triplet excitons and using a distributed feedback cavity with a high-quality factor, the authors realized stable green lasers based on quasi-2D perovskite under a continuous-wave optical pumping in air at room temperature (Fig. 1).

Singlet and triplet excitons usually co-exist in organic semiconductors, among which triplet excitons are poorly emitting. Moreover, triplet states may interact with the emitting singlet states causing energy loss in both of the states. In a previous work, Qin et al. [12] discovered that the lifetimes of triplet excitons could be as long as 1 μs in quasi-2D perovskites. In this regard, the authors speculated that the lasing death phenomenon may be caused by the presence of long-lived triplet excitons and associated singlet–triplet exciton annihilation.

To study the role of triplet excitons, Qin et al. [11] investigated $FAPbBr_3$-based (FA, formamidinium) quasi-2D perovskite films composed of two different organic cations, which were phenylethylammonium bromide (PEABr) and 1-naphthylmethylamine bromide (NMABr). Due to its lower energy of triplet excited state, NMA can readily quench the triplet excitons in N2F8 (i.e., Wannier excitons in $[PbBr6]^{4-}$ and triplet excitons in N2F8) through efficient triplet–triplet Dexter energy transfer. On the other hand, triplet excitons in P2F8 cannot be quenched by PEA due to its higher energy of triplet excited state. The ASE of P2F8 degrades gradually in nitrogen under continuous excitation because of the accumulation of long-lived triplet excitons, which leads to a reduced number of photons through singlet–triplet exciton annihilation. Triplet excitons can be quenched by oxygen or organic molecules with low energies. So the ASE intensity of P2F8 films remains unchanged in oxygen or ambient air and the emission intensity of N2F8 films is stable when pumped in different atmospheres. These findings demonstrate that triplet excitons in quasi-2D perovskites are detrimental for ASE, and triplet quenchers need to be introduced to obtain sustainable ASE or lasing from quasi-2D perovskites.

Qin et al. [11] then fabricated surface-emitting lasers by coating quasi-2D perovskite films onto substrates with grating structures that support second-order distributed feedback (Fig. 1b). Stimulated emissions ranging from 548 to 568 nm can be achieved by controlling the grating period (Λ) and film thickness. The emission features a narrow linewidth, a clear threshold, and an output beam characteristic of the resonator, confirming the formation of a laser. On the other hand, the lasing intensity of P2F8 decreased gradually and the emission eventually disappeared with the injection of nitrogen. The lasing can be recovered to the original intensity by quenching the triplet excitons with oxygen. These findings further confirm that triplet excitons are deleterious to the population inversion.

P2F8 and N2F8 DFB lasers were also demonstrated to operate successfully under CW pumping in air (Fig. 1c). Thresholds of the CW lasers based on P2F8 and N2F8 are respectively 59 and 45 W cm^{-2}, which are one or two orders magnitude lower than those under pulsed pumps. The reduced threshold under CW pumping is attributed to the different pumping wavelengths and the up-converting of partial triplet excitons into singlet states that contribute to the lasing action. When projected on a white paper, the output beam of the laser showed a fan shape with intense

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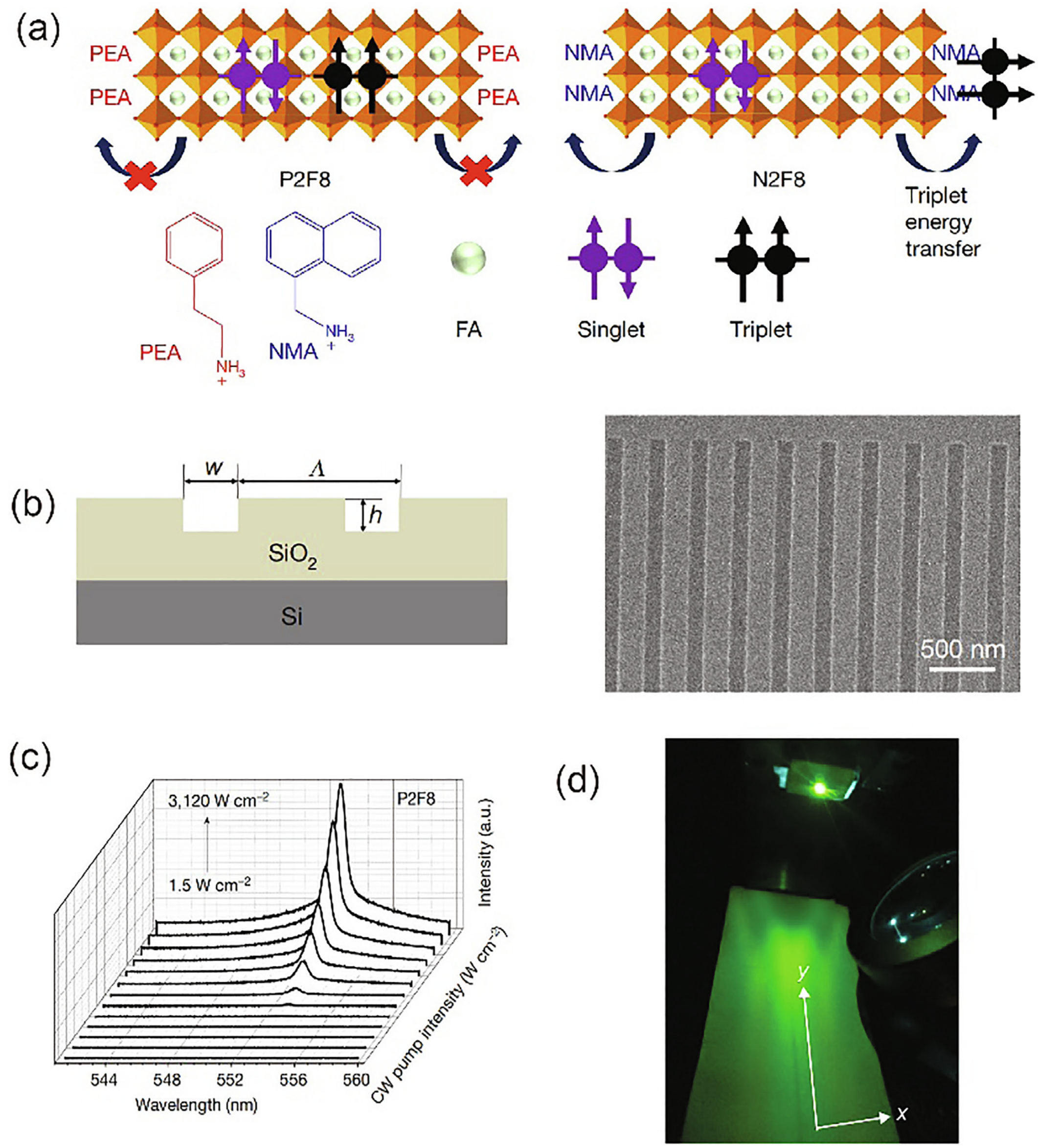

Fig. 1. (Color online) Chemical structures, DFB cavity, and continuous lasing properties of P2F8 and N2F8 films. (a) Chemical structure of qusi-2D perovskites with two different organic cations. Triplet energy transfer occurs from N2F8 to MMA, but no energy transfer from P2F8 to PEA. (b) Pattern design (left) and top-view scanning electron microscopy image (right) of a DFB cavity with air-trench width $w = 120$ nm, grating period $\Lambda = 250$ nm, and grating height $h = 60$ nm. (c) Emission spectra of P2F8 laser under CW excitation at different powers. (d) Photograph of the far filed pattern of CW lasing. Copyright © 2020, Springer Nature.

central double-lobed lines (Fig. 1d). Additionally, the CW lasing of P2F8 exhibited a strong linear transverse electric polarization. More impressively, lasing behaviors (intensity, FWHM, and wavelength) of P2F8-based laser were almost unchanged after continuous pumping for 1 h in air with a relative humidity of 55%, demonstrating excellent stability under CW operation.

Triplet excitons are easily quenched by oxygen. However, lasing death phenomenon was observed in a number of previous lasing measurements that were carried out in air. Therefore, more efforts should be devoted to investigating whether other factors (e.g., 2D structure) are required to realize CW lasing by quenching long-lived triplet excitons. To pave the way for further fabrication of electrically pumped lasers that are required in practical settings, several other challenges are to be overcome. For example, the optical gain of perovskite should be further improved. According the threshold of optically pumped perovskite lasers, the theoretical threshold of current density for eclectically injected lasing far exceeds the capabilities of typical perovskite electroluminescence devices in current use. Besides, the thermal conductivity of halide perovskite is one or two orders of magnitude lower than that of conventional inorganic semiconductors [13], leading to heat accumulation in the perovskite active layer under continuous electrically pumping.

In summary, the authors reveal that the lasing death phenomenon is ascribe to singlet–triplet exciton annihilation originated from long-lived triplet excitons and demonstrate the significance of managing triplet excitons in realizing continuous-wave lasers based on quasi-2D perovskites. This study is expected to promote the development of electrically driven laser devices based on perovskite with high efficiency, tunable operating wavelength, and solution processability at a low cost.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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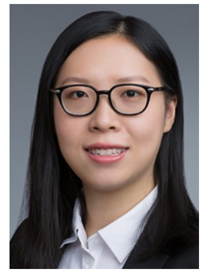

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