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Hybrid Plasmonic Surface Lattice Resonance Perovskite Lasers on Silver Nanoparticle Arrays

Zhen-Ting Huang, Chih-Wei Yin, Yu-Heng Hong, Heng Li, Kuo-Bin Hong, Tsung Sheng Kao, Min-Hsiung Shih, and Tien-Chang Lu*

The hybrid plasmonic surface lattice resonance (SLR) laser constructed by a MAPbBr₃ perovskite thin film on the Ag nanoparticle array is unambiguously demonstrated in this research. The relatively high refractive index of the perovskite thin film provides an excellent coupling between the photonic mode and SLR, leading to a high spontaneous emission coupling factor and a low threshold lasing. Furthermore, a novel spin-coating process applied to grow the MAPbBr₃ perovskite thin film can leave air gaps under the perovskite that provides a large index difference in the periodic array, making the hybrid plasmonic SLR exhibits a high density of state, which is beneficial for laser operation. Via theoretical design and experimental verification, the lasing behaviors of the hybrid plasmonic SLR perovskite laser show excellent characteristics with a fixed polarization. This demonstration facilitates an enhanced lasing performance and realization of the low-cost and low-energy-consumption laser application.

1. Introduction

Combining the dielectric and metal enables to form the oscillating electrons with the electromagnetic wave, called surface plasmon, introducing a localized electromagnetic wave at the interface. When the incident photon couples with this localized field, the mode volume will shrink significantly and then break the diffraction limit. This coupled quasi-particle is known as surface plasmon polariton, which has already been applied to break the diffraction limit. This coupled quasi-particle is known as surface plasmon polariton, which has already been applied in many optical nanodevices recently. Among them, the collective oscillation of an array of metallic nanoparticles called surface lattice resonance (SLR) exhibits an excellent capability to improve the resolution of the optical signal. Compared to the localized surface plasmon resonance (LSPR) in a single metallic nanoparticle, SLR with a high density of state (DOS) and low optical loss is beneficial to efficiently couple with the incoming wave and form the Fano resonance, which can dramatically shrink the linewidth of the output signal. Consequently, applying SLR as the operation mode is served as a useful method to realize the high-performance laser or intriguingly collective phenomenon, such as the ultralow threshold lasing by enhancing the Purcell effect, and steerable laser emission angle by changing the periodicity of SLR to other high-symmetry points. Notably, when it comes to the light–matter interaction, it is intuitive to associate with the Purcell factor, which is a critical parameter in the Purcell effect to estimate the increment of the spontaneous emission rate in the gain medium. In essence, the overlap between the optical field and the gain medium is proportional to the Purcell factor, which represents the larger the field-matter overlap is, the stronger the Purcell effect will be, resulting in more spontaneous emission coupling to stimulated emission and achieving a low threshold lasing performance. Therefore, to increase the field-matter overlap, a hybrid plasmonic mode is usually utilized in the design of plasmonic lasers. The hybridization between the plasmonic mode and photonic mode dramatically reduces the internal loss and improves the quality factor. More importantly, if the photonic mode is contributed from the waveguide mode formed in the gain medium, the field-matter overlap will strikingly increase, leading to a strong light–matter interaction. As a consequence, combining SLR with the waveguide mode is one of the solutions to overcome the limitation of light–matter interaction.

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interaction, and this hybrid plasmonic SLR mode shows the great potential to improve the characteristics of lasers and achieve outstanding lasing performance.

To design the hybrid plasmonic SLR mode, a perovskite thin film of methylammonium lead bromide (CH$_3$NH$_3$PbBr$_3$ or MAPbBr$_3$) is chosen in this work. In recent years, the hybrid organic-inorganic metal-halide perovskite materials have attracted much attention and have been applied in many states of the art optical devices, such as solar cells,[23] light emitting diodes,[24,25] and lasers.[26,27] With its high photoluminescence quantum efficiency and characteristics of tunable wavelength by changing the material composition, perovskite becomes a popular option in the gain materials for realization of visible wavelength band lasers.[26,28,29] Furthermore, via the solution-processable fabrication and a dripping technique during a spin-coating process, a high-quality perovskite thin film with extraordinary power conversion efficiency can be easily synthesized.[30,31] Accordingly, combining a metallic nanoparticle array with a perovskite thin film is a good choice to construct an outstanding but low-cost platform, which supports the hybrid plasmonic SLR mode, and the characteristic of strong light-matter interaction is beneficial to the laser application.

In this research, we fabricated MAPbBr$_3$ perovskite thin films on the silver (Ag) nanoparticle array protected by an aluminum oxide (Al$_2$O$_3$) passivation layer. Through properly design the array parameters, the hybrid plasmonic SLR mode was tuned to match the green light emission of the perovskite material. By optically pumping this structure, the hybrid plasmonic SLR mode was formed and oscillated to reach the threshold condition. Owing to the strong light–matter interaction, an excellent lasing performance can be observed by measuring the pumping threshold and fitting the spontaneous emission coupling factor $\beta$. More importantly, this demonstration of enhancing the light–matter interaction of SLR provides the promising characteristics of low-cost and low-energy consumption for practical application of optical devices.

2. Results and Discussion

Figure 1a shows the schematic diagram of our proposed hybrid plasmonic perovskite laser, which contains a 200 nm thick MAPbBr$_3$ perovskite thin film, a 10 nm thick Al$_2$O$_3$ passivation layer, a 30 nm thick Ag nanoparticle array, and a glass substrate. This structure supports the hybrid plasmonic SLR mode with different diffraction orders, which can be determined by the coupling direction of the electric or magnetic dipole and need to satisfy the following equation:[32,33]

$$\vec{k}_{inc} + i\vec{G}_x + j\vec{G}_y = \vec{k}_{i,j}$$

where $\vec{k}_{inc}$ and $\vec{k}_{i,j}$ represent the in-plane wave vector of the incident and diffractive wave, respectively, $\vec{G}$ is the reciprocal lattice vector. $i$ and $j$ indicate the diffraction order in the $x$- and $y$-direction. Hence, SLR($i$, $j$) can be used to denote the hybrid plasmonic SLR mode with a specific diffraction order. For example, the diffraction order of SLR(1,0) is in the $x$-direction, which
means the electric dipole or magnetic dipole couples along the x-direction. Besides, from Equation (1), when the in-plane wave vector of the incident wave is parallel to the direction of the diffraction order, this wave vector will contribute to the diffractive wave and then affect its eigenenergy according to its dispersion. The energy–wavenumber (E–K) diagram is demonstrated to prove this phenomenon by simulating the absorbance map as shown in Figure 1b,c, where the period in the x-direction ($\Lambda_x$) and y-direction ($\Lambda_y$), the filling factor in the x-direction ($f_{xx}$) and y-direction ($f_{yy}$) are originally set to be 285 nm, 285 nm, 0.16, and 0.65, respectively. Notably, at $\Gamma$ point of the square lattice in Figure 1b, SLR(1,0) and (-1,0) are slightly split due to the coupling between these two modes. The splitting energy depends on the coupling strength between the SLR mode and nanoparticle array.[34] When the incident wave inclines toward the x-direction, SLR(1,0) and (-1,0) gradually depart from each other and follow two linear functions along $k_y$, indicating two opposite propagating diffraction SLR waves. As it can been seen in Figure 1b, SLR(1, 0) and (-1, 0) belong to the bright and dark mode, respectively, due to their different parties.[34] On the other hand, SLR(0, 1) and SLR(0, -1) are also slightly split at $\Gamma$ point as shown in Figure 1c and gradually depart from each other and follow two linear functions along $k_x$. Therefore, SLR($\pm$1, 0) and SLR(0, $\pm$1) would show no dispersion along $k_y$ and $k_x$ directions in a small wave vector range, respectively. The frequency difference between SLR($\pm$1, 0) and SLR(0, $\pm$1) is due to the different geometric parameters of Ag nanoparticle along x and y directions. Again, only SLR(0, 1) but not SLR(0, -1) is observed because it belongs to the bright SLR mode.

In order to select the target operation mode, a confinement factor that defines the energy in the perovskite thin film over the whole energy of the SLR mode is considered, and the comparison between SLR(1, 0) and (0, 1) changed with $f_{xx}$ is shown in Figure 1d. Basically, the higher confinement factor implies there’s more optical field in the gain medium, resulting in a stronger light-matter interaction. The period in the x- and y-direction are also slightly shifted to make the wavelength of SLR near the perovskite emission wavelength. In our calculation, the confinement factor of SLR(0, 1) reaches as high as 0.92, which is higher than SLR(1, 0). Consequently, SLR(0,1) is chosen to become the target operational mode in our design, which is expected to have a lower lasing threshold due to the strong light-matter interaction. And the electric field distribution of SLR(0, 1) in the x- and z-plane is also shown in Figure 1e,f.

Furthermore, to find the optimal size of geometry for the laser cavity, firstly, the filling factors in the x- and y-direction are tuned to obtain a narrow linewidth of SLR(0, 1). The narrow linewidth implies a large quality factor and is beneficial for improving the lasing performance. Figure 2a shows the absorbance map as functions of $f_{xx}$ and the incident photon energy, where $\Lambda_x$, $\Lambda_y$, and $f_{yy}$ are fixed as 295 nm, 270 nm, and 0.65, respectively. Obviously, the energy of SLR(1, 0) and SLR(0, 1) are dramatically changed with $f_{xx}$, and their linewidth becomes narrower as $f_{xx}$ is smaller. By considering the limit of nanofabrication resolution, the $f_{xx}$ is set to be 0.16. Besides, $f_{xx}$ slightly affects the properties of SLR(0, 1) in the range between 0.3 to 0.7 in our calculation. $\Lambda_x$ is responsible for tuning the wavelength of SLR(0, 1) to match the peak emission wavelength of perovskite (=543 nm). According to the calculated absorbance map in Figure 2b, which fixes $f_{xx}$ as 0.65, the target $\Lambda_x$ is chosen as 270 nm, and the corresponding E–K diagram is shown in Figure 2c. Distinctly, SLR(0, 1) is located between SLR(1, 0) and SLR(-1, 0), and the density of state becomes the largest at $\Gamma$ point. The optimal design of our hybrid plasmonic perovskite laser is then determined and ready for the fabrication process. Besides, the schematic diagram of the final design with the detailed size is also shown in Figure S4 (Supporting Information).

To realize the hybrid plasmonic SLR mode, the fabrication of high-quality Ag nanoparticle arrays is essential because interface between Ag and perovskite is directly related to the surface scattering and dramatically affects the lasing threshold.[15] And a high-quality perovskite thin film is also pivotal. Additionally, the air gap under the perovskite thin film provides a large difference in refractive index, leading to enhancement of the coupling between periods and achieving a large density of state. The optical microscope (OM) image of the Ag nanoparticle arrays is shown in Figure 3a. The samples labeled as different numbers correspond to a continuous variation of $\Lambda_x$ and $\Lambda_y$. Among them, the scanning electron microscope (SEM) image of sample 5-1 is shown in Figure 3c. However, due to the imperfect fabrication, the actual $f_{xx}$ is larger than the design value, which is shifted from 0.16 to 0.23. When this shift is considered in our simulation, the target $\Lambda_x$ is changed from 270 to 263 nm. Hence, continuously varying the period in fabrication can prevent this kind of distortion and complete our design. Subsequently, a two-step spin coating process is used to grow the dense and uniform MAPbBr$_3$ perovskite thin film.[29,36]

More importantly, to fabricate the perovskite layer right on top
of the Ag nanoparticle array, the dynamic-dripping method for the spin-coating process is also utilized, and the OM image after spin-coating is shown in Figure 3b. To ensure the thickness of perovskite, the SEM image of the sample’s cross-section is taken and demonstrated in Figure 3d, where an approximate 200 nm thick perovskite film was grown successfully. The cross-section of the Ag nanoparticle array etched by focused ion beam (FIB) is exhibited in Figure 3e. The indicated air hole proves the perovskite thin film right on top of the Ag nanoparticle array can be fabricated by applying the dynamic-dripping method. The detailed fabrication process is discussed in Experimental section.

After sample preparation, the SLR mode is investigated by performing the transmission measurement before coating the MAPbBr₃ perovskite thin film to see the optical response with different periods of the metallic array. Figure 4a,b shows the experimental and simulated transmission spectra of different samples indicated in Figure 3a, respectively. In sample 5-1 to 5-6, Λₓ is changed from 300 to 310 nm, and Λᵧ is changed from 263 to 283 nm. For SLR(0, 1), the resonant wavelength is less sensitive to the variation of Λₓ but will change with Λᵧ. Therefore, in comparison to the experimental data, the transmission dip of SLR(0, 1) in simulation is shifted around 14 nm, which is pretty close to the 13.95 nm shown in our measurement. Figure 4c exhibits the power-dependent photoluminescence (PL) spectra of sample 5-1, and there is a striking peak appeared at 543 nm, which quite approaches the emission wavelength of perovskite. Additionally, the light-in versus light-out (L-L) curve is shown in Figure 4d. The pumping threshold (Pₜₜ) is around 0.54 μW, and the linewidth of lasing signal is only 0.28 nm. When the pumping power is gradually increased and up to 4 μW, the perovskite thin film starts to degrade, which is due to the thermal accumulation from the optical pumping and leads to a significant decay in the lasing intensity. This light-induced thermal degradation can be commonly observed in perovskite solar cells. Moreover, by fitting with simplified rate equations, the spontaneous emission coupling factor (β) of perovskite can be determined. Owing to the strong light-matter interaction, β of the hybrid plasmonic SLR mode is as high as 0.11, which is larger than those reported SLR lasers.

In addition to sample 5-1, the lasing behaviors of other samples are measured and discussed in detail. Λₓ of sample 6-1, 6-2, and 6-3 indicated in Figure 5a are 263.5, 264.3, and 265.7 nm, respectively. Other geometric parameters including Λᵧ, ffₓ, and ffᵧ in sample 6-1, 6-2, and 6-3 are almost the same as sample 5-1. Notably, according to the PL spectra in Figure 5a, where the pumping power was fixed at 1.2 × Pₜₜ, this slight offset of Λᵧ makes the lasing wavelength shift around 3 nm. Besides, to verify all the lasing signals belong to the same SLR mode, the corresponding far-field polarization is measured and demonstrated in Figure 5b. Evidently, the far-field polarization directions in these three samples are all the same and along the x-direction, which matches the simulated polarization discussed in Figure 2. Moreover, the relation between Pₜₜ and Λᵧ is exhibited in Figure 5c. As Λᵧ becomes larger, Pₜₜ significantly increases, which is because the lasing wavelength is gradually far from the gain peak of perovskite. Figure 5d shows the simulated absorption map as functions of Λᵧ and incident wavelength. The cyan dash line indicates the variation of SLR(0, 1) as Λᵧ is changed, and its slope (ΔΛ/ΔΛᵧ) equals 1.4, which is pretty close to 1.38 calculated by the difference of lasing wavelength divided by the shift of Λᵧ in Figure 5a. Consequently, by this comparison, it can be confirmed the lasing behavior observed in our measurement comes from the hybrid plasmonic SLR mode.
Figure 4. Optical characteristics of the hybrid plasmonic SLR mode. Before coating the perovskite thin film, the a) experimental and b) simulated transmittance spectra are demonstrated and compared with each other. In sample 5-1 to 5-6, \((\Lambda_x, \Lambda_y)\) is (300 nm, 263 nm), (303 nm, 267 nm), (305 nm, 271 nm), (308 nm, 275 nm), (310 nm, 279 nm), and (313 nm, 283 nm), respectively. After spin-coating, c) the power-dependent photoluminescence (PL) spectra of sample 5-1 is measured. Then the lasing wavelength can be determined to be 543 nm. d) The corresponding light-in versus light-out (L-L) curve and the linewidth of the emission peak as a function of pumping power, in which the black solid line is the fitting curve from simplified rate equations.

Figure 5. The lasing characteristics of the hybrid plasmonic SLR mode in different \(\Lambda_y\). a) The PL spectra in sample 6-1, 6-2, and 6-3, whose \(\Lambda_y\) are 263.5 nm, 264.3 nm, and 265.7 nm, respectively, and the pumping power is fixed as 1.2 \(\times P_{th}\). The green solid line is the normalized PL signal from the perovskite without Ag nanoparticle array. b) The corresponding far-field polarizations for sample 6-1, 6-2, and 6-3. c) The measured threshold power as a function of \(\Lambda_y\). d) The simulated absorbance map as functions of the incident wavelength and \(\Lambda_y\). The cyan dash line shows the variation of SLR(0, 1), and the black dash line shows the variation of SLR(1, 0).
Figure 6a,b demonstrates the temperature-dependent PL spectra below and above the lasing threshold, respectively. From 80 to 171 K, the PL peak shown in Figure 6a exhibits a blue-shifted trend, which is owing to a tetragonal-to-orthorhombic phase transition. When the pumping power closes to the lasing threshold, two amplified spontaneous emission (ASE) peaks appear in the spectrum. Among them, the peak with a shorter wavelength belongs to the random lasing signals. The formation of random lasing results from scattering through the inevitable grain boundaries produced by the spin-coating process, which implies the oscillation of random lasing does not originate from a well-defined cavity. Therefore, the observed random lasing peaks would follow with the PL gain peak, resulting in a blue shift as the temperature rises. In contrast, another peak belongs to the SLR lasing and shows a red-shifted trend from 80 to 171 K, which is due to the increment of refractive index in perovskite as temperature increases. We also place perovskite microplates on Ag nanoparticle arrays but only the whispering-gallery lasing mode is observed. The detailed analysis about random lasing and whispering-gallery-mode lasing of perovskite is discussed in Supporting Information.

3. Conclusion

A hybrid plasmonic SLR perovskite laser was architected by growing a MAPbBr₃ perovskite thin film on the Ag nanoparticle array. Through a series of theoretical designs and discussions, SLR[0, 1] with a confinement factor as high as 0.92 was chosen as the target cavity mode in order to intensively couple the optical field with the perovskite thin film and to achieve a strong light-matter interaction. Furthermore, a dynamic-dipping method for the spin-coating process was applied to the growth of MAPbBr₃ perovskite that leaves the air gap under the perovskite thin film for further improving the DOS of SLR mode. Subsequently, the lasing behaviors of the hybrid plasmonic SLR were determined by optical pumping. With a proper design, the optical pumping threshold of this plasmonic SLR laser is around 0.54 µW, and the lasing wavelength is 543 nm, which is pretty closed to the gain peak of perovskite.

4. Experimental Section

Sample Preparation: An electron beam lithography (EBL) and a lift-off process were applied to fabricate the high-quality Ag nanoparticle arrays. First, acetone, isopropanol (IPA), and water were used to clean the glass substrate, and then gently blow-dried it with nitrogen. Subsequently, a positive photoresist of poly-methyl methacrylate (PMMA) and an e-spacer were coated at 3500 and 2500 rpm, respectively. After prebake, an exposure process was applied by irradiating the electron beam, and the sample was soaked in the water to remove the e-spacer. Afterward, the solvent mixed by methyl isobutyl ketone (MIBK) and IPA with the mixing ratio of 7:3 was utilized to perform the development. Next, an e-gun evaporator was used to evaporate 50 Å Ti and 300 Å Ag. After evaporation, the sample was placed into acetone for lift-off process by using the ultrasonic cleaning for 5 s. Then the fabrication of the Ag nanoparticle array was finished. Additionally, to protect from naturally vulcanizing, atomic layer deposition (ALD) was used to deposit a 10 nm thick Al₂O₃ passivation layer. Hereafter, a spin-coating process was applied to grow the perovskite thin film. A powder comprised of methylammonium bromide (MABr) and lead bromide (PbBr₂) was dissolved into the solvent mixed by γ-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) with a mixing ratio of 7:3 at first. Then this solution was dynamically dripped onto our sample at 1000 rpm for 10 s. Second, the rotational velocity was raised up to 5000 rpm for 50 s. In the fabrication process, antisolvent toluene was also dripped onto the sample to facilitate the crystallization. Finally, after annealing at 100 °C for 30 min, a 200 nm perovskite thin was successfully fabricated.

Optical Measurement Setup: The sample was placed in a cryogenic chamber with pressure below 10⁻⁶ bar, and the temperature can be tuned from 77 to 300 K. The sample was pumped by a 532 nm pulse laser with a repetition rate of 1 kHz and a pulse duration of 0.35 ns. By passing through a 100 × infinity-corrected objective lens with a numerical aperture of 0.55 (Mitutoyo, Japan) and a working distance of 11 mm, the laser was focused on our sample, and the diameter of the pumping spot was approximately 15 µm. Then a nitrogen-cooled charge-coupled device attached to a 320 mm long single monochromator (iHR320, Horiba) was used to detect the lasing signals.
Simulations of Laser Characteristics: All the simulations including the absorption map, transmission spectra, and the electric field distribution were calculated by using the frequency domain solver of the finite-element software (COMSOL Multiphysics). Besides, the $\beta$ factor was obtained by fitting with simplified rate equations,[7] which is shown as follows:

$$\frac{dn}{dt} = \eta P - An - g_e(n - n_e)b$$  \hspace{1cm} (2)

$$\frac{db}{dt} = \Gamma B n + \Gamma g_e(n - n_e)b - \gamma b$$  \hspace{1cm} (3)

where $n$, $b$, $\eta$, $P$, $n_e$, $g_e$, and $\gamma$ is the carrier density, photon density, injection efficiency of excitons, pumping power density, transparency carrier density, differential gain, and radiation loss, respectively. $A$ is the average spontaneous emission rate of perovskite, which can be determined by the average spontaneous emission rate of perovskite, which can be obtained by fitting with simplified rate equations,[7] which is shown as follows:

$$\frac{dn}{dt} = \eta P - An - g_e(n - n_e)b$$  \hspace{1cm} (2)

$$\frac{db}{dt} = \Gamma B n + \Gamma g_e(n - n_e)b - \gamma b$$  \hspace{1cm} (3)

where $n$, $b$, $\eta$, $P$, $n_e$, $g_e$, and $\gamma$ is the carrier density, photon density, injection efficiency of excitons, pumping power density, transparency carrier density, differential gain, and radiation loss, respectively. $A$ is the average spontaneous emission rate of perovskite, which can be determined by $F/t$, where $F$ and $t$, are the Purcell factor of our hybrid plasmonic SLR mode and the spontaneous lifetime of perovskite. By solving the simultaneous differential equations shown in Equations (2) and (3), $\beta$ of the hybrid plasmonic SLR laser mode can be obtained. The detailed calculation parameters are indicated in Table S1 (Supporting Information).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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