Supplementary Information for

Metallic Cavity Nanolasers at the Visible Wavelength Based on In Situ Solution Grown Au-coated Perovskite Nanowires†

Xiaohao Jia,‡[a,b] Jian Wang,‡[c,d] Zhitao Huang,[a,b] Kaiwen Chu,[a,b] Kuankuan Ren,[e] Mingfei Sun,[a,b] Zhijie Wang,*[a,b] Peng Jin,*[c,d] Kong Liu,[a,b] and Shengchun Qu*[a,b]

[a.] Key Laboratory of Semiconductor Materials Science and Beijing Key Laboratory of Low Dimensional Semiconductor Materials and Devices, Institute of Semiconductors, Chinese Academy of Science, Beijing,100083, China.

[b.] Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China.

[c.] School of Instrumentation Science and Engineering, Harbin Institute of Technology, Harbin 150001, China.

[d.] Key Laboratory of Micro-systems and Micro-structures Manufacturing (Harbin Institute of Technology), Ministry of Education, Harbin 150080, China.

[e.] School of Mathematical Information, Shaoxing University, Shaoxing, 312000, China.

Section 1: The reaction mechanism of Au-$CH_3NH_3PbBr_3$ nanowires.

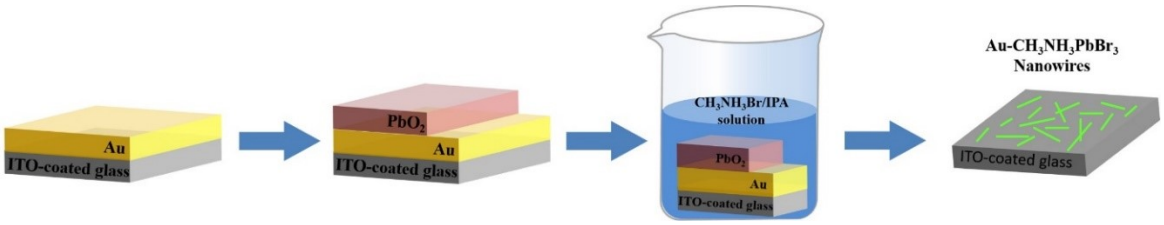

Fig. S1. Synthesis process of Au-$CH_3NH_3PbBr_3$ nanowires. The Au films and the PbO_2 films were deposited on the ITO glass substrates by a clever design, and reacted with 0.2 mg mL^{-1}~10 mg mL^{-1} CH_3NH_3Br isopropyl alcohol solutions for 10 min ~ 4 h to obtain the Au-$CH_3NH_3PbBr_3$ nanowires.

The as-grown Au-$CH_3NH_3PbBr_3$ nanowires were synthesized by a modified solution method,[1] as Fig. S1 schematically illustrated. First, the gold thin film was deposited on the ITO-coated glass substrate by the evaporation method. Then, the as-grown gold thin film was partially covered with the PbO_2 film prepared by the electrochemical deposition. The tentatively exposed gold film could participate in the reaction for the growth of Au-$CH_3NH_3PbBr_3$ nanowires.[2] Immersed in the CH_3NH_3Br isopropanol solution, the PbO_2 films were primarily converted to $CH_3NH_3PbBr_3$ nanowires as follows (Equations 1-3):[3]

$$CH_3NH_3Br \leftrightarrow CH_3NH_2 + HBr \quad (1)$$

$$PbO_2 + 4HBr \rightarrow PbBr_2 + 2H_2O + Br_2 \quad (2)$$

$$PbBr_2 + CH_3NH_3Br \rightarrow CH_3NH_3PbBr_3 \quad (3)$$

Initially, the CH_3NH_3Br decomposed to CH_3NH_2 and HBr in the isopropanol solvent, which was a reversible reaction. Afterwards, the generated HBr reacted with the immersed PbO_2 quickly to form $PbBr_2$, accompanied by the generation of H_2O and Br_2, and then the $PbBr_2$ continued to react with CH_3NH_3Br to synthesize $CH_3NH_3PbBr_3$. As the reaction went on, plenty of intermediate products like HBr, Br_2 and H_2O formed, which would assist the dissolution of the gold films as follows.

Because the bromide ions, not only act as strong ligand of Au^+ and Au^{3+}, but also possess high oxidation potential under acidic condition, the dissolution mechanism of gold by bromide can be discussed from two aspects.[2] Firstly, the gold could be oxidized by bromide ions to $AuBr_2^-$ (Equation 4). While the $AuBr_2^-$ is unstable, and then disproportionates to stable $AuBr_4^-$ and Au (Equations 5). This process can be represented by the reactions as:[4]

$$Au + 2Br^- \leftrightarrow AuBr_2^- + e^- \quad (4)$$

$$3AuBr_2^- \leftrightarrow AuBr_4^- + 2Au + 2Br^- \quad (5)$$

Secondly, the gold could be oxidized to $AuBr_4^-$ directly, which could be represented by the reaction (Equations 6):[5]

$$2Au + 3Br_2 + 2Br^- \leftrightarrow 2AuBr_4^- \quad (6)$$

The Br_2 can be hydrolyzed to form the hypobromous acid. And then the gold is oxidized by the hypobromous acid. Thus the Equation 6 can be described by the following detailed reactions (Equations 7-8),[6] where the gold is oxidized by the Br_2 and complexed by bromide ions.

$$Br_2 + H_2O \leftrightarrow HOBr + H^+ + Br^- \quad (7)$$

$$2Au + 3HOBr + 5Br^- + 3H^+ \leftrightarrow 2AuBr_4^- + 3H_2O \quad (8)$$

Assisted by the intermediate products from the growth process of $CH_3NH_3PbBr_3$, the dissolution of gold occurs after the synthesis of $CH_3NH_3PbBr_3$ nanowires. Then we can introduce gold to the surface of $CH_3NH_3PbBr_3$ nanowires, since the bromide ions on the surface of $CH_3NH_3PbBr_3$ nanowires could complex with gold ions. All these chemical reactions about the dissolution of gold are reversible in the solution, causing the co-existence of $AuBr_2^-$, $AuBr_4^-$ and Au on the surface of Au-$CH_3NH_3PbBr_3$ nanowires.

After the Au/PbO_2 films reacted with CH_3NH_3Br isopropanol solution for 2-4 hours, the as-grown samples were put on a hot plate at 50 °C for 5 min, which made the gold complex turn into stable form of Au. Compared with perovskite grown on the ITO-coated glass without gold films in our previous work, the optimal reaction time changes from 4 hours to 2 hours, which proves that the consumption of the intermediate products accelerates the reaction process.[7] Ultimately, we obtained the $CH_3NH_3PbBr_3$ nanowires encapsulated by the gold thin layers, defined as Au-$CH_3NH_3PbBr_3$ nanowires. Specifically, the metallic cavity nanolasers in this work are based on the Au-$CH_3NH_3PbBr_3$ nanowires with five surfaces coated by gold films, because

the transfer process would strip the as-grown nanowires away from the ITO-coated glass to the SiO_2 substrate, causing one side broken off.

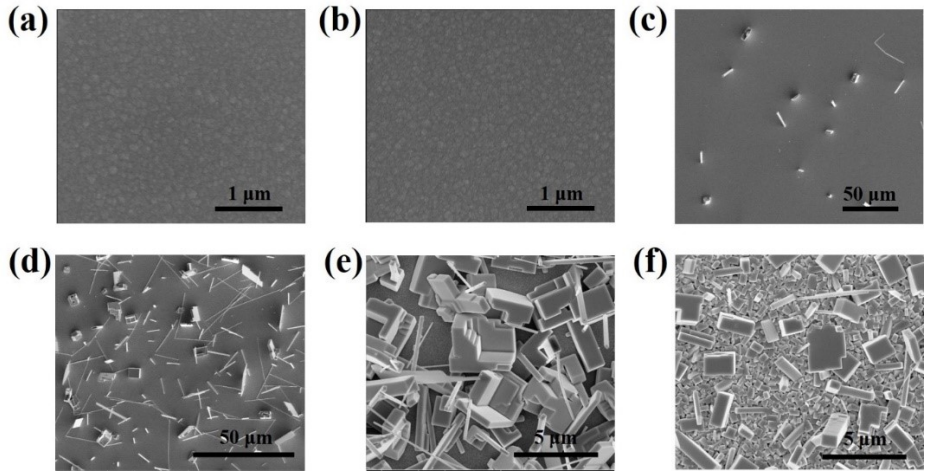

Fig. S2. The SEM images of Au-$CH_3NH_3PbBr_3$ nanowires grown at various concentrations of CH_3NH_3Br isopropyl alcohol solutions. (a) 0.2 mg mL^{-1}, (b) 0.5 mg mL^{-1}, (c) 1 mg mL^{-1}, (d) 2 mg mL^{-1}, (e) 5 mg mL^{-1}, (f) 10 mg mL^{-1}.

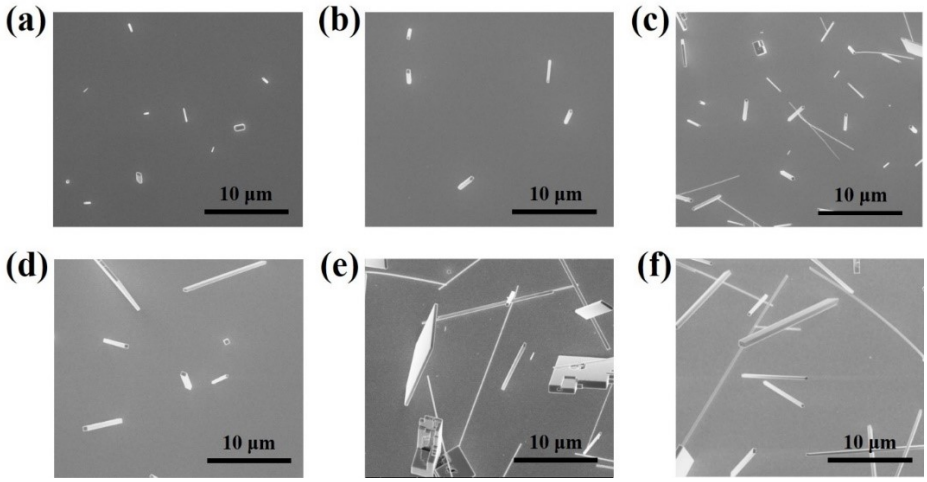

Fig. S3. The SEM images of Au-$CH_3NH_3PbBr_3$ nanowires grown at 2 mg mL^{-1} CH_3NH_3Br isopropyl alcohol solutions for various reaction time. (a) 10 min, (b) 30 min, (c) 1 h, (d) 2 h, (e) 3 h, (f) 4 h.

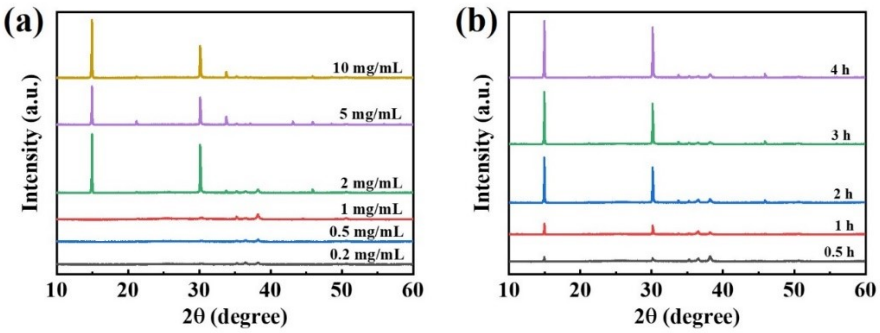

Fig. S4. The XRD patterns of Au-$CH_3NH_3PbBr_3$ nanowires grown at (a) various concentrations of CH_3NH_3Br isopropyl alcohol solutions and (b) various reaction times.

Section 2: The numerical and experimental results of the devices.

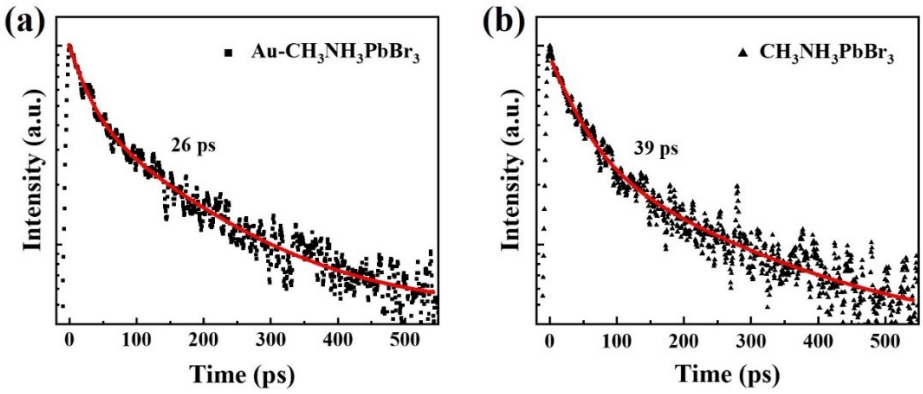

Fig. S5. The time-resolved photoluminescence decay (TRPL) of the (a) Au-$CH_3NH_3PbBr_3$ nanolasers and (b) $CH_3NH_3PbBr_3$ nanolasers at high excitation density (1 P_{th}).

	Material	τ_1 (ϕ_1)	τ_2 (ϕ_2)	τ_{ave}
Spontaneous Emission	Au-$CH_3NH_3PbBr_3$	1.06 ns (72.81%)	6.13 ns (27.19%)	2.44 ns
	$CH_3NH_3PbBr_3$	6.13 ns (41.99%)	10.98 ns (58.01%)	8.94 ns
Stimulated Emission	Au-$CH_3NH_3PbBr_3$	26 ps (99.98%)	145 ps (0.02%)	26 ps
	$CH_3NH_3PbBr_3$	39 ps (98.20%)	200 ps (1.80%)	42 ps

Table S1. The TRPL fitting parameters at the spontaneous emission and the stimulated emission. The biexponential decay curves are fitting by $I(t) = A_1 exp\left(\frac{t}{\tau_1}\right) + A_2 exp\left(\frac{t}{\tau_2}\right)$, where τ_1 and τ_2 are the first lifetime and the second lifetime. The ϕ1 and ϕ2 are the proportion of the τ_1 and τ_2, defined as $\varphi_1 = \frac{A_1\tau_1}{A_1\tau_1 + A_2\tau_2}$ and $\varphi_2 = \frac{A_2\tau_2}{A_1\tau_1 + A_2\tau_2}$. The τ_{ave} is the average lifetime calculated by $\tau_{ave} = \tau_1\varphi_1 + \tau_2\varphi_2$.

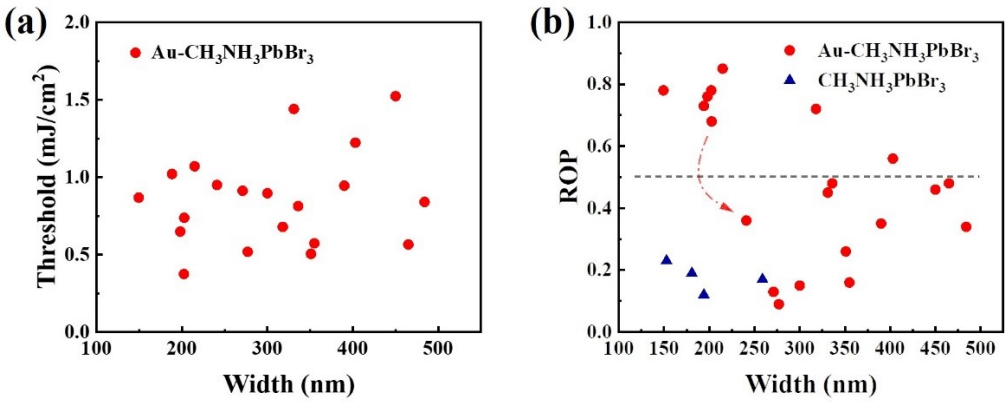

Fig. S6. The (a) threshold and (b) ROP value against the width of the nanowires.

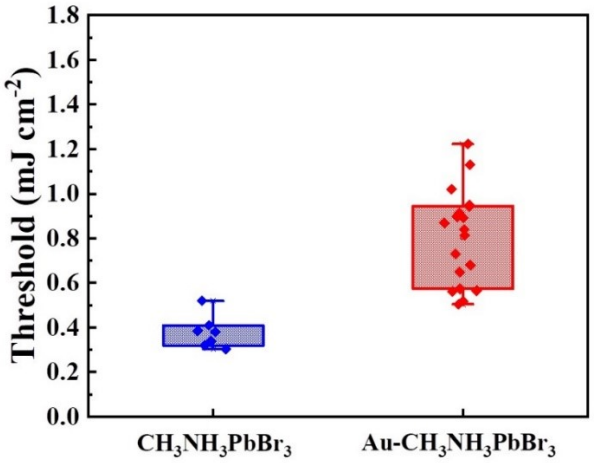

Fig. S7. The box chart of threshold of the $CH_3NH_3PbBr_3$ nanolasers and Au-$CH_3NH_3PbBr_3$ nanolasers.

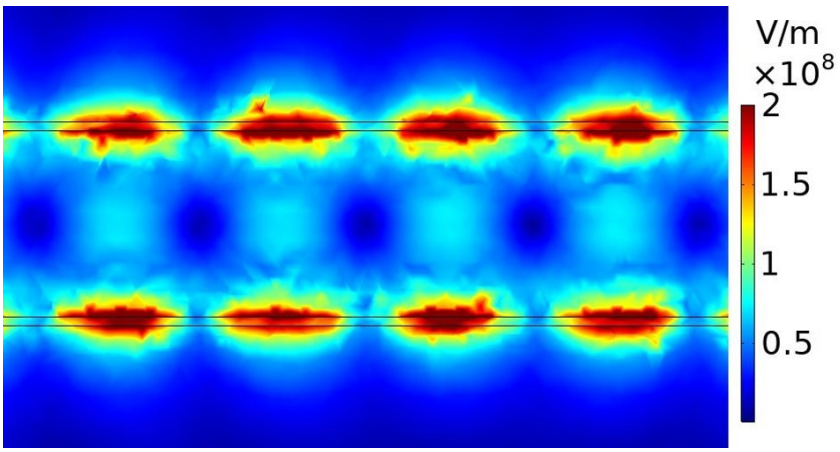

Fig. S8. Top-view calculated electric field distribution of Au-$CH_3NH_3PbBr_3$ nanolasers at the interface of Au shell and $CH_3NH_3PbBr_3$.

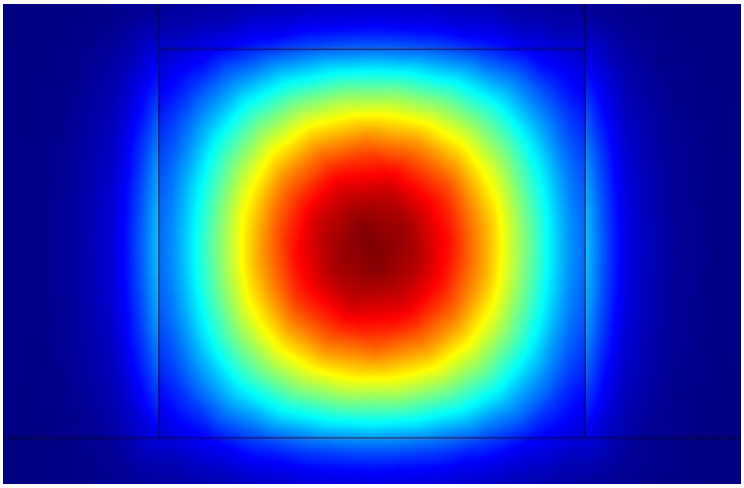

Fig. S9. Calculated electric field distribution of $CH_3NH_3PbBr_3$ nanolasers with nanowire width of 500 nm.

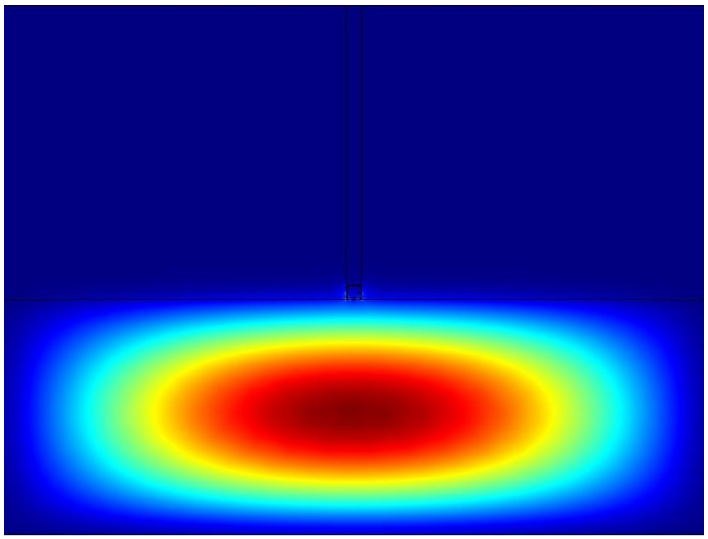

Fig. S10. Calculated electric field distribution of Au-$CH_3NH_3PbBr_3$ nanolasers with nanowire width of 100 nm.

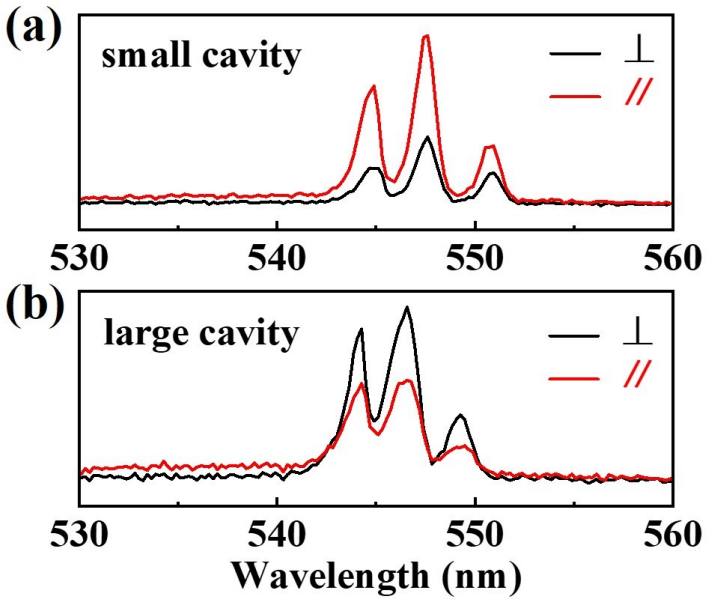

Fig. S11. The polarization property of Au-$CH_3NH_3PbBr_3$ nanolasers with small size (150 nm) and large size (400 nm).

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