

Au-Seeded CsPbI₃ Nanowire Optoelectronics via Exothermic Nucleation

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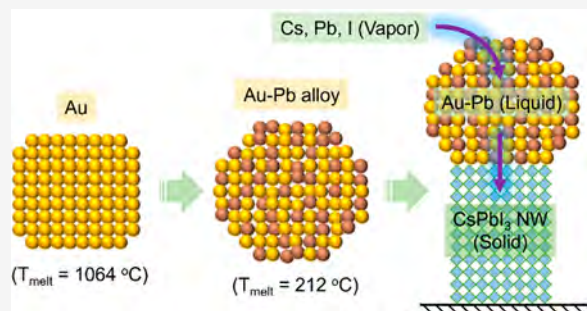
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ABSTRACT: Converting vapor precursors to solid nanostructures via a liquid noble-metal seed is a common vapor deposition principle. However, such a noble-metal-seeded process is excluded from the crystalline halide perovskite synthesis, mainly hindered by the growth mechanism shortness. Herein, powered by a spontaneous exothermic nucleation process ($\Delta H < 0$), the Au-seeded CsPbI₃ nanowires (NWs) growth is realized based on a vapor–liquid–solid (VLS) growth mode. It is energetically favored that the Au seeds are reacted with a Pb vapor precursor to form molten Au–Pb droplets at temperatures down to 212 °C, further triggering the low-temperature VLS growth of CsPbI₃ NWs. More importantly, this Au-seeded process reduces in-bandgap trap states and consequently avoids Shockley–Read–Hall recombination, contributing to outstanding photodetector performances. Our work extends the powerful Au-seeded VLS growth mode to the emerging halide perovskites, which will facilitate their nanostructures with tailored material properties.

KEYWORDS: vapor–liquid–solid synthesis, Au seeds, CsPbI₃ nanowires, exothermic nucleation, optoelectronics



Crystalline halide perovskites (HPs) produced by chemical vapor deposition (CVD) could serve as perfect platforms for exploring their fundamental physical properties and practical device implementations.^{1–4} Compared with the solution synthesis processes, the CVD methods are better for controlling the geometry of HP nanostructures, such as diameter, length, shape, and phase.^{5,6} To date, the most used CVD-based growth technique for HP synthesis is the vapor–solid (VS) process, in which the vapor-phase precursor is converted to a solid product via surface adsorption.^{7–10} This way, the yielded VS-HP nanostructures are determined by the crystal surface energy and substrate feature. For instance, sapphire,⁷ mica,⁸ and SrTiO₃¹⁰ were used to grow all-inorganic HP nanostructures with specific crystallographic orientations. At the same time, the high growth temperature, stringent substrate requirement, and elusive heteroepitaxial relationships are always involved in the VS process, which may impose constraints on the material synthesis and further utilization.

Alternatively, the vapor–liquid–solid (VLS) process is more attractive for achieving controllable growth and bottom-up synthesis of integration-ready nanostructures.¹¹ In the VLS mode, nanostructures are precipitated from the supersaturated molten seeds. As for the catalytic seeds, noble metals (e.g., Au, Pd, and Pt) are commonly used due to the minimal lattice diffusion.^{12,13} Importantly, the VLS-grown all-inorganic CsPbX₃ (X = Cl, Br, or I) HP nanowires (NWs) and core–shell perovskite NWs were demonstrated recently,^{14,15} in

which Sn nanoparticles were used as catalytic seeds due to their low melting temperature (232 °C) and good compatibility to Pb-based HPs.¹⁶ Although such pioneering works highlight the potential of VLS-HP synthesis, it was achieved at the expense of the Sn impurity atom diffusion into HP host lattices. As a result, this could deteriorate the material homogeneities regarding phase purity, surface morphology, and electrical characteristics.¹⁷ To eliminate such impurity doping, utilizing typical noble metals to seed the VLS growth of HP NWs is a feasible route.

Herein, using noble-metal Au as catalytic seeds, all-inorganic CsPbI₃ NWs are VLS grown on amorphous SiO₂/Si substrates. The formation enthalpy of Au–Pb catalytic seeds is found to be negative ($\Delta H < 0$), which means the formation of Au–Pb eutectic is a spontaneous exothermic nucleation process. In an energetically favored way, the Pb vapor would react with Au seeds to form molten Au–Pb droplets, with corresponding melting temperatures decreasing from 1062 to 212 °C. The formation of these molten droplets mediates the efficient VLS growth of CsPbI₃ NWs at low temperatures. More notably, the

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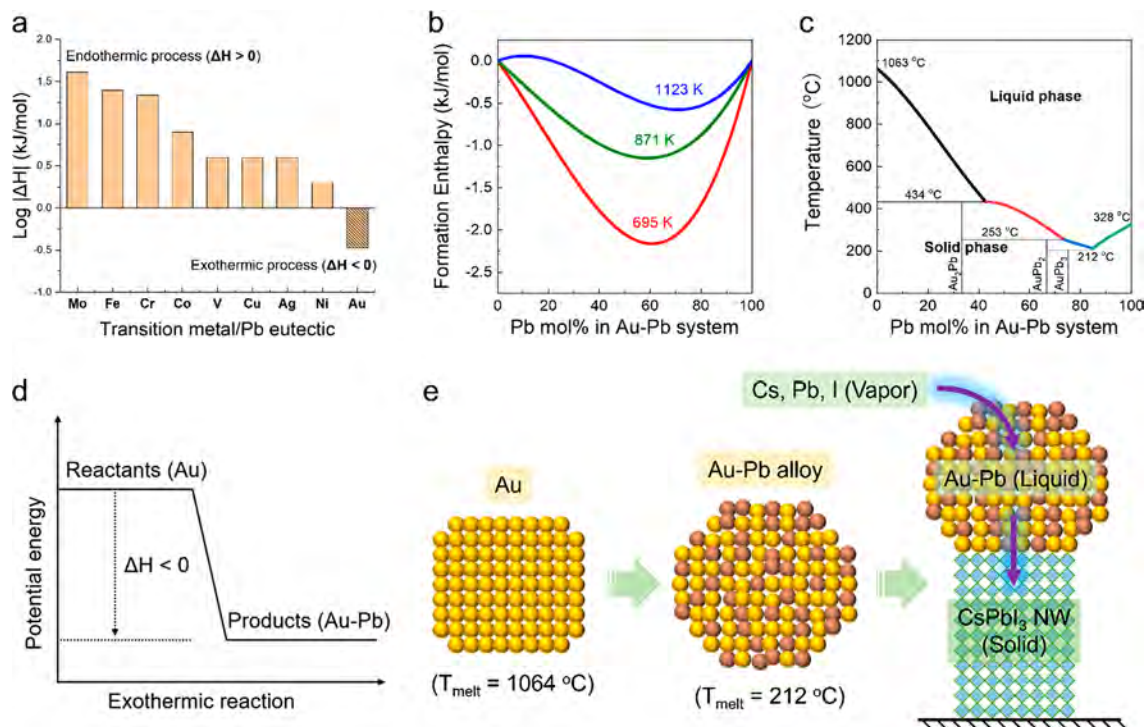


Figure 1. (a) Formation enthalpy of transition metals/Pb alloying systems with equiatomic compounds ratios. (b) The formation enthalpy of the Au–Pb alloying system as a function of composition ratio under different temperatures. (c) The phase diagram of the Au–Pb system. (d) The exothermic process of the Au–Pb alloying process. (e) Schematic diagram of the enthalpy-mediated Au-seeded growth of CsPbI₃ perovskite NWs.

Au-seeded process prevents the in-bandgap trap states generated in CsPbI₃ NWs, giving rise to enhanced intrinsic material properties and superior photodetector performances, including an average responsivity of 1350 A·W⁻¹ and a specific detectivity of 1.8 × 10¹⁴ Jones.

The eutectic alloying of catalytic seeds is the prerequisite for VLS growth. In this work, a semiempirical model is investigated to shed light on the eutectic alloying kinetics of the Au–Pb system. In general, the energy associated with eutectic alloying is mainly used to change the boundary conditions to form new binary compounds.¹⁸ When two metals come in contact, the metal with high chemical potential would transfer the electrons to the low potential metal side. If taking the concentration dependence, volume effect, and electron density difference into further consideration, the formation enthalpy (ΔH) values of eutectic alloying could be estimated by the full expression as (details can be found in [Supporting Information Text 1](#))¹⁹

$$\Delta H = \frac{2Pf(C^s)(C_A V_A^{2/3} + C_B V_B^{2/3})}{(n_{WS}^A)^{-1/3} + (n_{WS}^B)^{-1/3}} \left[-(\Delta\phi^*)^2 + \frac{Q}{P}(\Delta n_{WS}^{1/3})^2 - \frac{R}{P} \right] \quad (1)$$

where $\Delta\phi^*$ is the work function difference ($\Delta\phi^* = \phi^{*A} - \phi^{*B}$) between two metals, and Δn_{ws} is the electron density difference ($\Delta n_{ws} = n_{ws}^A - n_{ws}^B$) at the Wigner–Seitz atomic cell boundaries. To realize the numerical evaluation of ΔH , the atom concentrations (C_A and C_B), molar volumes (V_A and V_B), and the surface concentrations (C^s) could be found elsewhere and considered as constants, while polarizability (P) and the parameter R (the larger the number of p-electrons in nontransition metal, the larger the R) are 12.3 and 2.1 for

alloys of a transition metal (i.e., Au) with a nontransition metal (i.e., Pb).^{18,19} To better show the influence factors, the ΔH could be approximately described by a simplified expression as

$$\Delta H \sim -P(\Delta\phi^*)^2 + Q(\Delta n_{WS}^{1/3})^2 - R \quad (2)$$

Obviously, when two metals are transformed into the binary eutectic alloy, the $\Delta\phi^*$ and Δn_{ws} between two metals would play crucial roles in such a eutectic alloying process.

Based on the semiempirical model, the ΔH values of Pb alloying with different transition metals (M) could be calculated. [Figure 1a](#) shows the ΔH of different M–Pb alloying systems with equiatomic compound ratios (i.e., M–Pb = 1:1). Unusually, among many M–Pb alloying systems, the ΔH of Au–Pb alloying is found to be negative, being minus 3 kJ/mol atoms, which means that the total energy of the products is less than the total energy of the reactants. This negative value is mainly because of the distinct work function difference between Au ($\phi^* = 5.10$ – 5.47 eV) and Pb ($\phi^* = 4.25$ eV), which generates a significant negative contribution to the formation energy. Also, the ΔH of the Au–Pb alloys as a function of composition are calculated at different temperatures ([Figure 1b](#)).²⁰ As the contact surface between dissimilar atoms changes with compositions, the nonsymmetrical concentration dependence of ΔH is hence observed. Anyway, the ΔH values of Au–Pb alloys are negative ($\Delta H < 0$) over the whole composition range and work well with temperatures up to 1123 K, which means the Au–Pb eutectic alloying is a spontaneous exothermic process. Importantly, the Au–Pb phase diagram in [Figure 1c](#) shows the significantly reducing melting temperature of Pb-rich Au–Pb catalyst seeds, potentially down to 212 °C.²¹ Overall, the spontaneous exothermic nucleation process and the low-melting temper-

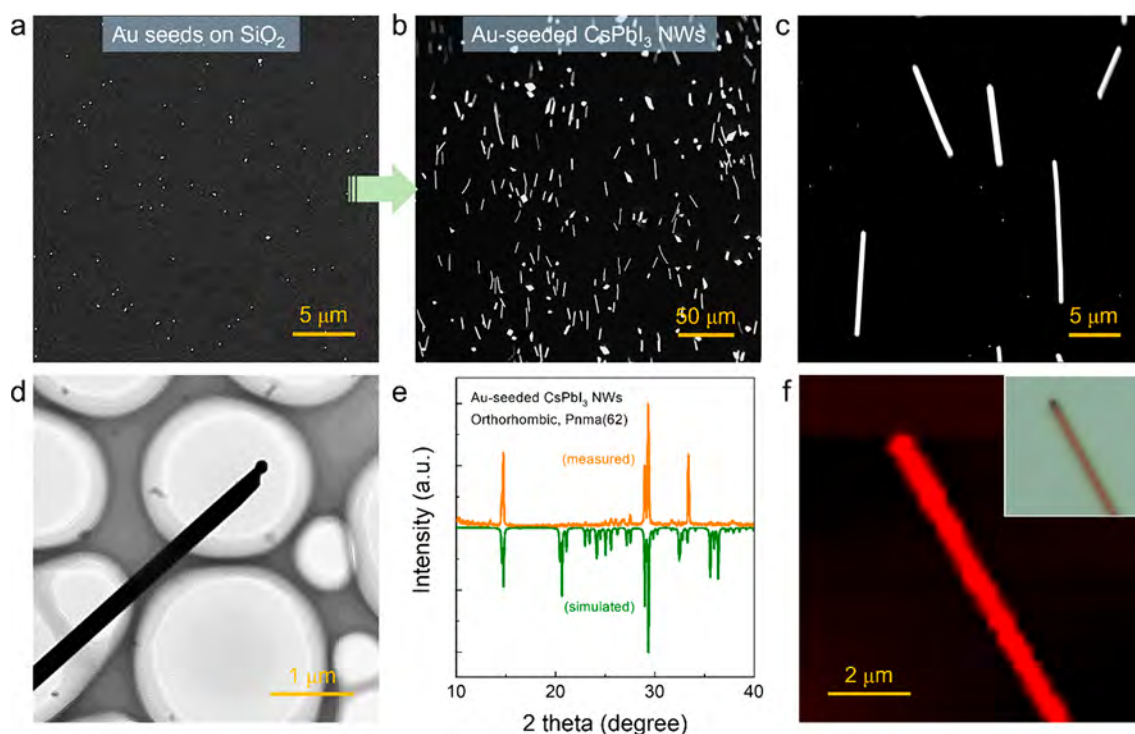


Figure 2. (a) SEM images of the Au nanoparticles drop-casted on amorphous SiO₂/Si substrates. (b,c) Titled SEM images of the Au-seeded VLS-grown CsPbI₃ NWs on substrates. (d) TEM image of individual CsPbI₃ NWs grown with Au catalytic seeds. (e) XRD pattern of Au-seeded VLS-grown CsPbI₃ NWs. (f) PL mapping and (inset) optical image of Au-seeded CsPbI₃ NWs.

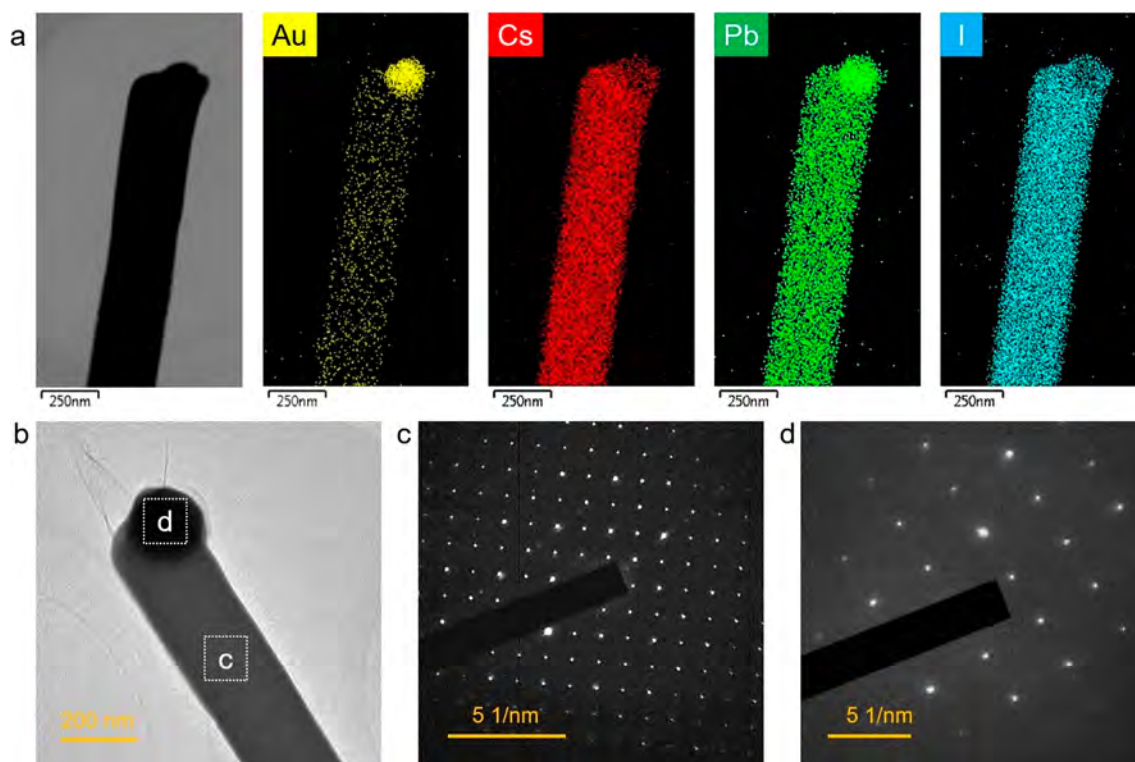


Figure 3. (a) Scanning TEM image and corresponding EDS mapping of a typical Au-seeded VLS-grown CsPbI₃ NW. (b) HRTEM image of the Au-seeded CsPbI₃ NW and corresponding SAED patterns of (c) the NW body region and (d) Au-Pb catalytic tip region.

atures of Au–Pb catalyst seeds would drive the VLS growth of CsPbI₃ NWs at low temperatures (Figures 1d and e).

To experimentally verify the above model, the CsPbI₃ NWs were synthesized via the Au-seeded growth process (details

shown in the Methods section and Figure S1). Briefly, in a two-zone CVD system, the mixed CsI/PbI₂ powder placed in the first heating zone (430 °C) was used to generate the vapor-phase source of Cs, Pb, and I. The growth substrates carrying

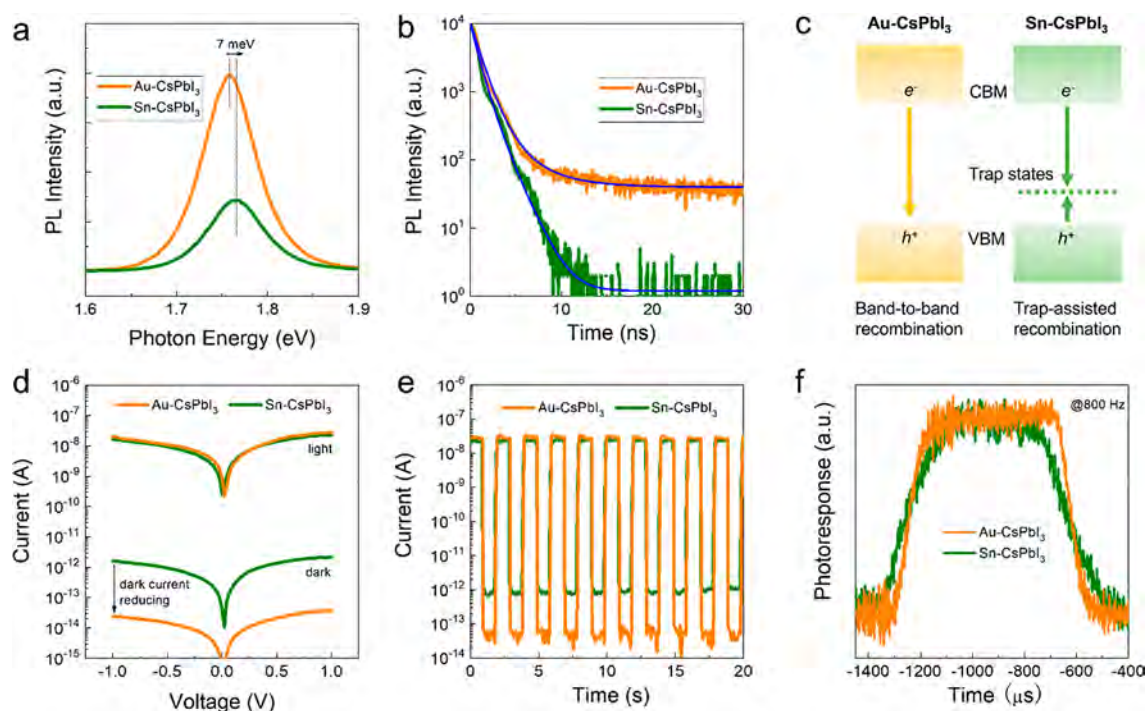


Figure 4. (a) PL spectra and (b) TRPL curves of the VLS-grown CsPbI₃ NWs using different catalytic seeds. (c) Energy band structures of VLS-grown CsPbI₃ NWs using different catalytic seeds. (d) *I*–*V* curves of CsPbI₃ NW PDs measured in 532 nm light and dark conditions. (e) *I*–*t* curves of CsPbI₃ NW PDs with 0.5 Hz chopping light illumination and 1 V bias. (f) Time-resolved photoresponse of the CsPbI₃ NW PDs measured at 800 Hz chopping frequency.

predeposited Au nanoparticles (Figures 2a and S2) were placed in the second heating zone (290 °C), where the heating temperature is significantly lower than the conventional VS synthesis of ~600 °C. With a growth pressure of 0.8 Torr and Ar carrier gas flow of 80 sccm, the Au nanoparticles could spontaneously alloy with Pb vapor and fully convert to Au–Pb catalytic seeds. Since the Au–Pb alloy has a melting temperature down to 212 °C (Figure 1c), the molten Au–Pb catalytic seeds at a set temperature of 290 °C are responsible for the CsPbI₃ NW growth. Indeed, holding the growth conditions for 120 min leads to a good yield of out-of-plane CsPbI₃ NWs on the amorphous SiO₂/Si substrate (Figures 2b, 2c, and S3). From the statistical analysis, the resulting CsPbI₃ NWs are 17.9 ± 1.5 μm in length and 193 ± 19 nm in diameter, exhibiting decent morphology uniformity. Also, the temperature-dependent and pressure-dependent growth is investigated to shed light on the controllable VLS growth of Au-seeded CsPbI₃ NWs (Figure S4 and Supporting InformationText 2). To show the generality, the Au-seeded VLS growth method was successfully optimized for the synthesis of CsPbBr₃ NWs (Figure S5).

As shown in the transmission electron microscopy (TEM) images in Figure 2d and Figure S6, all the NWs are terminated with characteristic spherical catalytic seeds, indicating this work's VLS growth process. Moreover, control experiments on SiO₂ substrates without predeposited Au seeds show no NW growth, confirming that Au seeds are necessary to trigger the NW growth on such amorphous substrates. To study the crystal structure, the X-ray diffraction (XRD) pattern was measured from Au-seeded CsPbI₃ NWs (Figure 2e). All the XRD peaks could be aligned to the orthorhombic CsPbI₃ (*Pnma* (62), *a* = 8.856 Å, *b* = 8.576 Å, *c* = 12.472 Å),^{14,22} corresponding to an adapted crystal structure of perovskite

featuring tilted [PbI₆]⁴⁻ octahedra. From the PL mapping result, the CsPbI₃ NW emits red light across the entire NW (Figure 2f), which also indicates the orthorhombic black phase of Au-seeded CsPbI₃ perovskite NWs, instead of the electronically inactive yellow δ-phase (nonperovskite phase) that possesses a wide bandgap of 2.7 eV. Notably, there are three black perovskite phases, including cubic (*α*-phase), tetragonal (*β*-phase), and orthorhombic (*γ*-phase), which are optically active and hence useful for solar cells, photodetectors, light-emitting diodes, etc.^{4,23} Due to the group–subgroup relations, the orthorhombic *Pnma* phase could be regarded as a pseudo cubic *Pm-3m* phase. Reversible phase transitions, induced by strain, thermal effect, and other effects, could further tune their crystallographic characteristics for advanced device applications in the future.^{24,25}

After that, the energy-dispersive X-ray spectroscopy (EDS) mapping was used to characterize the Au-seeded VLS-grown CsPbI₃ NW in detail (Figure 3a). Specifically, the NW tip mainly consists of Au and Pb elements (Figures S7 and S8), in which the relatively richer Pb part in the Au–Pb catalytic tip would lower the melting temperature potentially down to 212 °C.²¹ When heating to a growth temperature (i.e., 290 °C), the molten Au–Pb seeds would act as a preferential adsorption position for the incoming vapor sources until a supersaturation condition is reached. A small amount of Cs and I elements in the NW tip is also witnessed from EDS mapping, revealing their precipitation priority in the supersaturation process. This is mainly because of the low equilibrium solubility of Cs and I in Au as well as the high melting point of their eutectic alloys, e.g., 1070 °C of Au₅Cs.^{26,27} Thus, based on the EDS result and thermal analysis, the VLS growth of Au-seeded CsPbI₃ NWs is driven by the efficient supersaturation of Cs and I in a liquid catalyst. Besides, the component quantification is also

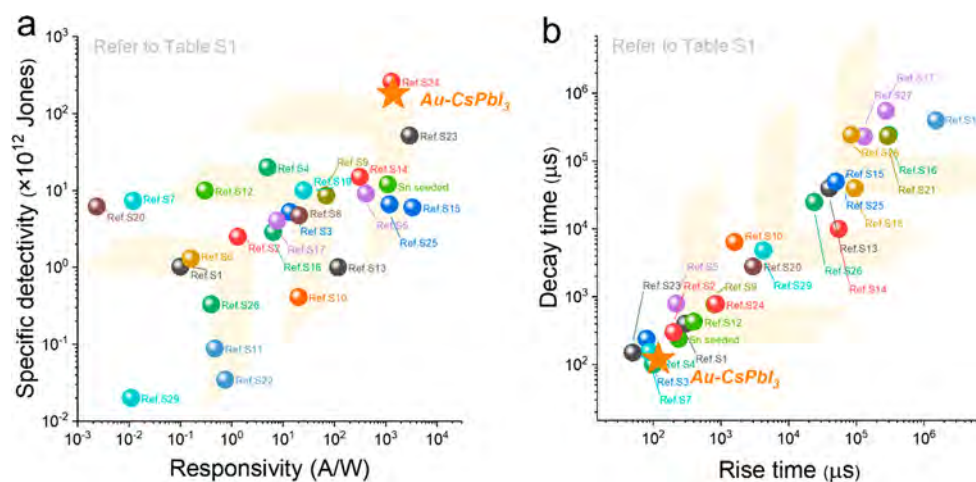


Figure 5. PD performance comparisons of the perovskite NWs, including (a) responsivity, specific detectivity, (b) rise time, and decay time. Detailed performance parameters are shown in Table S1.

conducted on the CsPbI₃ NW body (Figure 3a), which highlights the uniform distribution of Cs, Pb, and I elements on the NW body with an ideal composition ratio of 1:1:3 (Figure S8). Also, X-ray photoelectron spectroscopy (XPS) demonstrated the typical chemical states of CsPbI₃ materials with distinctive characteristic peaks, which could be assigned to the core levels of Cs 3d, Pb 4f, and I 3d (Figure S9).

The crystal structure of the CsPbI₃ NWs was further evaluated through high-resolution TEM and selected-area electron diffraction (SAED) in Figures 3b–3d. The SAED pattern of the catalytic tip is indexed to be AuPb₃ eutectic (Figure 3d), which is different from the polycrystalline Sn-based catalytic tip with nanoscale dendrite formation (Figure S10 and Supporting InformationText 3). From the Au–Pb phase diagram in Figure 1c, the Pb-rich compositions show relatively low melting temperatures among the whole composition range. This fact benefits the low-temperature VLS growth of perovskite NWs in this work since the molten Au–Pb seeds at growth conditions are needed. Besides, the SAED pattern of the NW body is indexed to be an orthorhombic phase (Figure 3c), which agrees well with the XRD results in Figure 2e. For CsPbI₃ NWs in this work, their orthorhombic perovskite structure is thermally stable at room temperature because of the larger I[−] ionic radius than other halogens that induce the structural adaptation.^{22,23} Besides, based on the SAED pattern, the Au-seeded CsPbI₃ NWs prefer to grow along the [100] direction, consistent with the reported observations and computations.^{14,28} The (100) planes of CsPbI₃ NWs have lower surface free energy than other planes, driving the preferred directional crystal growth. Overall, the above structure and element analysis conclude that the CsPbI₃ NWs are growing via a supersaturation process at the molten Au–Pb seeds, following the VLS mechanism.

Understanding the impurity doping of perovskites is critical to control their electrical properties for device applications. To this aim, the photoluminescence (PL) spectra were collected and compared between Sn-seeded and Au-seeded CsPbI₃ NWs (Figure 4a). The Au-seeded CsPbI₃ NW has a full emission width at half-maximum of 110 meV centered at 1.76 eV. It is repeatable that the emission peak of Sn-seeded CsPbI₃ NWs shows a 6–14 meV left blue shift compared to the Au-seeded CsPbI₃ NWs (more micro-PL spectra could be found in Figure S11). In the literature, it has been experimentally and

theoretically verified that the CsPbX₃ lattice would contract due to the incorporation of the smaller guest cations, like Sn²⁺, Cd²⁺, and Zn²⁺ guest cations.²⁹ Also, the electronic structure calculations performed on 240 perovskites have clearly shown that the bandgaps of perovskites would increase with the decreasing unit cell volume and/or with the increasing electronegativity (EN) of constituent species.³⁰ From a viewpoint of the different radii (*r*) and electronic configurations of Pb²⁺ ([5d¹⁰6s²6p⁰], *r* = 119 pm, EN = 1.6) and Sn²⁺ ([4d¹⁰5s²5p⁰], *r* = 112 pm, EN = 1.7), the observed blue-shift emission is primarily related to the Sn impurity doping and the lattice contraction.^{29,31} The EDS mapping of Sn-seeded CsPbI₃ NWs indicates the diffusion of Sn element into the NW body during the VLS growth process (Figure S12). Based on the EDS mapping and reported findings elsewhere,³² the Au elements also existed in the NW body, yet appearing in an optically inactive manner possibly because the Au-based defect energy levels are out of the forbidden region. Thus, the Au-seeded CsPbI₃ growth avoids the in-bandgap trap states as a contrast to the Sn-seeded sample (Figure 4c), which is supported by electronic structure calculations in Figure S13 based on first-principles density functional theory (DFT).

To further investigate the impurity doping effect on CsPbI₃ NWs, time-resolved PL (TRPL) measurements were performed on both Sn-seeded and Au-seeded samples. As shown in Figure 4b, the PL decay (average carrier lifetime) of the Sn-seeded CsPbI₃ NWs (0.68 ns) is faster than the Au-seeded one (1.92 ns). This finding indicates that the Sn incorporation indeed affects the intrinsic band structure of CsPbI₃ NWs. Typically, when electronic defects are introduced (such as impurities, vacancies, and interstitials) to a semiconductor, they offer localized trap states inside the band gap.³³ In the trap-assisted Shockley–Read–Hall recombination (SRH) process, these undesirable in-bandgap trapping states would act as recombination centers to capture photogenerated carriers and thus shorten their diffusion length, directly interfering with the operation of optoelectronic devices.¹⁷ Hence, in-bandgap traps are not appreciated in many optoelectronic devices as they may lead to poor performance and a large delay in photoresponse. In this regard, the unaltered electronic band structures of Au-seeded CsPbI₃ NWs may endow them with superior material properties, promising for high-speed optoelectronics.

Following that, individual CsPbI₃ NWs were configured into visible-light photodetectors (PDs) to demonstrate their optoelectronic applications.^{14,34} As shown in the current–voltage (*I*–*V*) curves in Figures 4d and S14, the Au-seeded CsPbI₃ NW PDs show ultralow dark currents (*I*_{dark}) below 0.1 pA biased at 1 V. When light illumination with an intensity of ~5 mW/cm² is applied, the light current (*I*_{light}) of Au-seeded CsPbI₃ NW devices increases by more than ~10⁶ times to 23.1 ± 1.8 nA, which is higher than the light/dark current ratio of Sn-seeded CsPbI₃ NW devices of ~10⁴ (Figure 4d and 4e). As shown in Figure S15, the noise current spectrum is dominated by the 1/*f* noise for both Au-CsPbI₃ NW and Sn-CsPbI₃ NW devices when biased at 1 V. Besides, there is a pronounced noise reduction from 6 fA/Hz^{1/2} of Sn-CsPbI₃ to 0.5 fA/Hz^{1/2} of Au-CsPbI₃ at 1 Hz, which can be ascribed to the introduction of Sn impurity dopants into the NWs. Because of the lower noise signal, the specific detectivity (*D*^{*}) of Au-seeded PDs is calculated to be 1.8 × 10¹⁴ Jones (cm·Hz^{1/2}W⁻¹), higher than Sn-seeded PDs of 1.2 × 10¹³ Jones, which outperforms most perovskite NW devices reported to date (Figure 5a and Table S1). The responsivity (*R*) is also an important figure-of-merit to evaluate PD performance. To be specific, the *R* value of Au-seeded CsPbI₃ NWs is as high as 1350 ± 110 A·W⁻¹ with an incident light intensity of 5 mW/cm², larger than that of Sn-seeded CsPbI₃ NWs of 1080 ± 120 A·W⁻¹ under the same conditions. The relatively smaller *R* value of Sn-seeded NWs could be attributed to the photocarrier loss via the nonradiative recombination at those impurity trap states.¹⁷

The transient response time is critical for PDs and highly depends on the efficient transport/collection of photo-generated carriers.^{35,36} A high-speed photoresponse measurement circuit, mainly composed of the current amplifier and digital oscilloscope, was built to record the dense photo-response signals chopped at 800 Hz.^{13,15} As shown in Figure 4f, the Au-seeded CsPbI₃ NW shows a faster photoresponse time of 120 μs when compared to Sn-seeded CsPbI₃ NWs of 240 μs and most reported perovskite NWs to date (Figure 5b and Table S1). The obtained faster photoresponse from Au-seeded CsPbI₃ NWs originated from the minimized in-bandgap traps. Due to the same reason, the Au-seeded CsPbI₃ NW PDs exhibit better stability than the Sn-seeded sample in the light/dark switching measurement (Figure S16), together with a good photoresponse covering the entire visible-light region (Figure S17).

In this work, noble metal Au catalyst seeds are first employed to trigger the VLS growth of crystalline CsPbI₃ NWs. Enabled by a spontaneous exothermic nucleation process, the VLS growth temperature is lowered to 290 °C, which is unachievable by conventional VS growth processes. Unlike other metal seeds like Sn, the Au-seeded process would not lead to impurity doping in the HP host lattice, thus eliminating the in-bandgap trap states. When configuring single CsPbI₃ NWs into PDs, excellent photodetector performances toward the visible-light regime were obtained, including an average responsivity of 1350 A·W⁻¹, a light/dark current ratio of ~10⁶, a detectivity of 1.8 × 10¹⁴ Jones, and a photoresponse time of 120 μs, better than most reported perovskite devices. Overall, the Au-seeded VLS HP growth process bridges one of the most powerful growth techniques with the emerging HP materials, promising for both fundamental and practical studies on low-dimensional HPs in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.2c03612>.

Methods section; SEM image of Au seeds; cross-section SEM, TEM, EDS, and XPS analysis of Au-CsPbI₃ NWs; temperature-dependent and pressure-dependent growth study of Au-CsPbI₃ NWs; SEM, PL, and EDS analysis of Au-CsPbBr₃ NWs; STEM image and EDS mapping of Sn-CsPbI₃ NWs; micro-PL spectra, calculated band structures, noise current spectrum, and photodetection performance of both Au- and Sn-CsPbI₃ NWs; photo-response as a function of operating time or light wavelength; performance summary of one-dimensional perovskite devices (PDF)

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Notes

The authors declare no competing financial interest.

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