

Increasing photoluminescence quantum yield by nanophotonic design of quantum-confined halide perovskite nanowire arrays

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ABSTRACT: High photoluminescence quantum yield (PLQY) is required to reach optimal performance in solar cells, lasers and light-emitting diodes (LEDs). Typically, PLQY can be increased by improving the material quality to reduce the non-radiative recombination rate. It is in principle equally effective to improve the optical design by nanostructuring a material to increase light out-coupling efficiency and introduce quantum confinement, both of which can increase the radiative recombination rate. However, increased surface recombination typically minimizes nanostructure gains in PLQY. Here a template guided vapor phase growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) nanowire (NW) arrays with unprecedented control of NW diameter from the bulk (250 nm) to the quantum confined regime (5.7 nm) is demonstrated, while simultaneously providing a low surface recombination velocity of 18 cm s^{-1} . This enables a 56-fold increase in the internal PLQY, from 0.81 % to 45.1 %, and a 2.3-fold increase in light out-coupling efficiency to increase the external PLQY by a factor of 130, from 0.33 % up to 42.6 %, exclusively using nanophotonic design.

The internal and external photoluminescence quantum yields (IPLQY and EPQLY) are defined as the ratio between the number of photons internally emitted and photons absorbed in the remote phosphor layer, and the ratio between the number of photons externally emitted and photons incident on the phosphor layer, separately. Considering the fact that IPLQY is determined by the relative rates of internal radiative and non-radiative recombination, which cannot be experimentally measured, it is thus more common to estimate it by using EPLQY and the light out-coupling efficiency. Hence, both the IPLQY and EPLQY play a key role in the performance of a wide variety of optoelectronic devices such as solar cells,^{1,2} light-emitting diodes (LEDs)³⁻⁵ and lasers⁶.

The common approach to increase PLQY is to improve material quality, which reduces the non-radiative recombination rate, for example by minimizing bulk,⁷ surface⁸ and interfacial⁹ defects. It is in principle also possible to increase PLQY solely via nanophotonic engineering, by increasing the absorption cross-section,¹⁰ light out-coupling¹¹ or quantum confinement¹². All of these strategies increase the radiative recombination rate, but very often the increase in surface recombination when nanostructuring a material plays a bigger role, leading to an overall loss in PLQY. In the most successful example so far, nanostructuring InP increased PLQY by a factor of 14 using a combination of increased absorption cross-section and light out-coupling.¹³ Such a large improvement was enabled by the very low native surface recombination velocity (SRV) of InP as well as its high refractive index, which leads to low light out-coupling efficiency (2 %) in planar wafers due to total internal reflection. Increasing light out-coupling has also been applied to halide perovskite materials, but the lower refractive index makes it more difficult to see an improvement – indeed only a factor of 3 has been observed so far.¹⁴ However, halide perovskites also have very low native SRV,¹⁵ making them an interesting candidate for studying radiative recombination rate enhancements

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3 via quantum confinement. Several studies have observed quantum confinement in
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7 colloidal halide perovskite nanowires (NWs).¹⁶⁻¹⁹ In one case, smaller diameters led to
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10 lower PLQY, showing that surface recombination dominated over the quantum
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13 confinement effect.¹⁶ In another example, a substantial increase in PLQY by a factor of 6
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16 was observed,¹⁷ but different synthetic conditions used to reach different NW diameters
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19 made it difficult to determine the relative effect of quantum confinement versus differences
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22 in material quality. Furthermore, colloidal systems are not suitable for most optoelectronic
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25 applications, where quantum wires (QWs) need to be in the solid-state in a geometry that
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28 allows for external contacting and efficient carry extraction/injection. It is thus an
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31 outstanding challenge to synthesize QWs with tunable diameters suitable for fundamental
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34 studies and optoelectronic device applications, while equally challenging is reaching
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37 sufficiently excellent surface passivation so that the change in radiative recombination
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40 rate rather than surface recombination dominates the PLQY.
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50 Here we tackle both the synthetic and surface passivation challenges enabling a high
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53 IPLQY (45.1 %) and a 130-fold increase in EPLQY only via reducing the NW diameter,
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by far the largest enhancement originating from quantum confinement and nanophotonic effects. We utilize porous alumina membranes (PAMs) as templates to fabricate ultra-high density ($\sim 10^{12} \text{ cm}^{-2}$) vertical $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) NW arrays with controllable and uniform diameters from $250 \pm 10 \text{ nm}$ down to $5.7 \pm 1.4 \text{ nm}$, all grown under the same vapor-solid-solid reaction (VSSR) conditions.²⁰⁻²² The processes for PAM formation, VSSR growth, photodetector fabrication, and extraction of QWs for transmission electron microscopy (TEM) characterization are shown schematically in Figure 1 (full details in Methods). Briefly, the nanoengineered PAMs are formed by electrochemical anodization of aluminum (Al) foil, with the pore diameters in nanometers approximately equal to the anodization voltage in Volts (Figure S1 and S2). Specifically, from the SEM images, it can be seen that the nanopores are semi-ordered on substrate with diameters of $5.7 \pm 1.4 \text{ nm}$, $9.1 \pm 1.0 \text{ nm}$, $12.2 \pm 1.8 \text{ nm}$ and $18.8 \pm 2.2 \text{ nm}$, respectively, which hence determine the diameters of both subsequently electrodeposited Pb NW precursor and the grown MAPbI_3 QWs. Meanwhile, the 5 V PAM has an ultra-high pore density which can be calculated as high as $\sim 1 \times 10^{12} \text{ cm}^{-2}$. This unique feature of PAM will consequently contribute to ultra-high density perovskite QW arrays with every single QW well isolated, which will be

extremely promising for the ultra-high resolution imaging or sensing applications in the future. After a barrier layer thinning process, metallic Pb is electrochemically deposited at the bottom of the PAM channels and subsequently converted to MAPbI₃ NW arrays using the VSSR process.²⁰ A variety of perovskite NWs can be obtained with a similar process simply by electrodepositing different metals at the bottom of the PAM or by using different powder precursors during the growth.^{21, 22} A low energy surface ion milling process is carried out to remove the unwanted layer of bulk polycrystalline MAPbI₃ on top of the PAM, leading to NWs with identical length in all PAM nanochannels. Afterwards, another short growth step using the same conditions is applied to repair the ion beam damaged surface. All optical measurements are performed on the arrays at this stage (Figure 1e). For the photodetector measurements, patterned indium-tin-oxide (ITO) contacts are sputtered on top of the NW arrays without further annealing process (Figure 1f).

Our previous reports have confirmed that a PAM can serve as an excellent packaging material for halide perovskite NWs, leading to the drastically improved stability against water, oxygen and spontaneous phase transformation.²⁰⁻²² This stability enhancement is

critical for device applications, however also makes it difficult to extract individual NW for TEM characterization. Since etching away the PAM with acids/bases would destroy the perovskite NW array, we instead mechanically grind the embedded array into a fine powder (Figure 1g) and subsequently sonicate it in chlorobenzene. The sonication extracts the NWs from the broken edges of the PAM and uniformly disperses them in the solvent (Figure 1h), enabling TEM characterization as well as future single QWs device fabrication and characterization.

High-resolution TEM (HRTEM) and X-ray diffraction (XRD) confirm that the MAPbI₃ NWs are monocrystalline (Figure 2). Interestingly, the XRD patterns are dominated by (100) planes matching with the pattern of standard cubic MAPbI₃, indicating the NWs have a cubic crystal structure,^{20,23} corresponding to the high temperature phase (>327 K) of bulk MAPbI₃.²⁴ The reason for this stable cubic phase rather than the tetragonal phase at room temperature can be attributed to the spatial confinement of the PAM template, which has already been confirmed on FAPbI₃ and CsPbI₃ NWs growth.^{22, 25} More specifically, cubic phase MAPbI₃ can be naturally obtained during the high temperature

(180 °C) growth.²⁴ Then, after finishing the growth and cooling down to the room temperature, the PAM template provides spacial confinement that prevents perovskite NWs from lattice distortion and volume expansion which are required for the transformation to tetragonal phase. Hence, the cubic phase of perovskite NWs in the PAM template is eventually stabilized at room temperature. It has been reported that crystallite size of nanocrystals can be estimated with XRD result by using Scherrer equation:²⁶

$$D = \frac{0.89\lambda}{B\cos\theta} , \tag{1}$$

where D is the average crystallite size, B and θ are respectively the full width at half-maximum (FWHM) and the angle of XRD peak, λ is the wavelength of the X-ray (0.154056 nm). From XRD results in Figure 2d, the FWHM values of (100) peak for QWs with diameters of 5.7 nm, 9.1 nm, 12.2 nm, and 18.8 nm are 0.474°, 0.385°, 0.383° and 0.326°, respectively. Therefore, the crystallite size of these four kinds of QWs can be calculated as 16.7 nm, 20.5 nm, 20.7 nm and 24.3 nm. Compared with the extracted diameters from SEM, the larger size values calculated from XRD can be attributed to the fact that each individual QWs have different growth orientations.²⁰ This can also be seen

from Figure 2d. When (100) plane are parallel to QW axial direction, the calculated crystallite size is equal to QW diameter. However, when (100) plane are perpendicular to QW axial direction, the calculated crystallite size is equal to QW length, namely 100 nm. Therefore, eventually the calculated nanocrystallite size is larger than the actual diameter of QWs. Nevertheless, the obvious decrease in signal intensity and comparative broadening of FWHM of the diffraction peaks is still consistent with the QW diameter reduction, as also observed in colloidal perovskite quantum dots (QDs)²⁷ and QWs¹⁶. From the HRTEM, it is clear that both the electrodeposited Pb and the converted MAPbI₃ NWs have the diameters determined entirely by the PAMs (Figure 2 and S3). The interplanar distance of ~0.63 nm corresponds to the (100) planes of cubic MAPbI₃, the same as observed in nanocrystals.²⁸

The absorption and PL spectra show that the 250 nm diameter NW arrays exhibit optical properties comparable to those of bulk MAPbI₃ (Figure 3a),²⁰ while as the diameter decreases towards the Bohr radius, the PL peak and absorption edge show a significant blue-shift, indicating bandgap widening due to quantum confinement. Especially,

compared with the PL peak and absorption edge of 772 nm for 250±10 nm diameter NW arrays, the 5.7±1.4 nm diameter QW arrays show a maximum blue shift of 59 nm (133 meV). Note that recently, a maximum 122 nm (301.5 meV) blue shift was observed from MAPbI₃ QDs with almost the same diameter (6.6±0.7 nm).²⁹ This discrepancy can be explained by the fact that QWs have only two-dimensional (2-D) confinement of excitons while QDs have three-dimensional (3-D) confinement.³⁰ Figure 3b quantitatively illustrates the dependence of optical bandgaps on the average NW diameters, calculated using the PL peak positions. The bandgap change (ΔE_g) shows an inverse square relationship ($\Delta E_g \propto 1/d^2$) to the diameter (d), consistent with the simple particle-in-a-box model for QWs:³⁰⁻³²

$$\Delta E_g = \frac{1.17h^2}{8d^2} \cdot \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) = \frac{1.17h^2}{8m^*d^2} = \frac{k}{d^2}, \quad (2)$$

where, h , m_e^* , m_h^* , and m^* represent Planck's constant and the electron, hole and reduced effective mass, respectively. Using the slope value (k) of 2.70 eV nm² extracted from the linear fitting (Figure 3b inset), the reduced effective mass m^* is estimated to be 0.16 m_0 , where m_0 is the free electron mass. This result is consistent with the reported

value of $0.15m_0$.³³ Time-resolved photoluminescence (TRPL) measurements show that smaller diameter NWs have faster PL decays (see Methods fitting details), corresponding to shorter carrier lifetimes (Figure 3c, Table 1). Typically, shorter carrier lifetime suggests more carrier recombination. Since there are mainly two routes of recombination, namely, radiative and non-radiative recombination, increase of either or both recombination rate can lead to a shorter carrier lifetime. Organometal perovskite materials are known to have low bulk defects thus bulk defect associated non-radiative recombination is low.¹⁵ Meanwhile, recently we have discovered that our PAMs provide excellent surface passivation to perovskite NWs thus SRV is very low.³⁴ One may consider that smaller QW diameter leads to larger surface-to-volume ratio and more severe surface non-radiative recombination, as observed in some inorganic NWs.^{35,36} However, smaller diameter NWs provided much stronger spacial confinement to the photogenerated excitons, as compared with larger diameter NWs. This increases radiative recombination rate in the smaller diameter NWs, as also reported in QD materials.³⁷ Therefore, we can draw a conclusion that short carrier lifetime is caused by increasing radiative recombination. This

argument can be further substantiated by the fact that the smaller diameter NWs/QWs have higher PLQY than large diameter NWs, which will be discussed in the following.

Figure 4a and b (left triangles) show that as the NW diameters decrease from 250 nm to 5.7 nm, the EPLQYs increase from 0.33 % to 42.6 %. In all cases, the EPLQYs are weakly dependent of excitation intensity, with a maximum enhancement by a factor 4 when changing the power intensity by 4 orders of magnitude. This suggests all NW samples are in the low-injection regime, where the background carrier density is much higher than the photogenerated carrier density.³ However, the situation is very different for the thin film, which not only shows a lower EPLQY (maximum of 0.1 %), but also a strong power dependence, approaching the linear scaling expected for films dominated by non-radiative recombination in the high injection regime.³⁸ The large difference likely arises from the different synthetic methods between the thin-film and NW arrays. The increase in PLQY with stronger quantum confinement suggests the origin of the improvement is an increased radiative recombination rate (nanophotonic effect), rather than a decreased non-radiative recombination rate (improved material quality). To obtain

the IPLQY values, we firstly simulated the light out-coupling efficiency of different dipoles polarizations (typically the vertical and horizontal dipoles) in the NW arrays using finite-difference time-domain (FDTD) method with simulation details and results shown in supplementary. However, a simple average of those two different polarization values, which is usually suitable for planar perovskite films,³⁹ is not the case in our QW arrays because the quantum confinement will bias the emission towards the dipole polarization direction with the strongest confinement and then alter the light out-coupling.⁴⁰ Hence, more precisely, we used the relative internal radiative recombination rate enhancement, which can be extracted by using the IPLQY and lifetime data, as the weighting factors for those two components. Then, a modified photon recycling model¹⁴ was used to calculate the IPLQY with the use of EPLQY and light out-coupling efficiency (OCE) with calculation details shown in supplementary. Generally, compared with 250 nm NW arrays, the OCE for 5.7 nm QW arrays shows a 2.3 times enhancement from 39.8 % to 90.6 %, as shown in Table 1 and Figure S6. Figure 4a and b (right triangles) show the power dependent IPLQYs for different NW arrays and thin films. Significantly, the EPLQY (42.6 %) for 5.7 nm QW arrays only show ~5 % lower than the IPLQY (45.1 %) which is mainly attributed

to the highly effective light out-coupling (90.6 %). However, this reduction is as low as 60 % for 250 nm NW arrays, and 96 % for thin films, which confirms the expectation that reducing NW diameter will enhance the light out-coupling.⁴¹ Figure 4c plots the internal and external radiative recombination rates versus the inverse NW diameter squared. The difference between those two rates shows the same trend with that of IPLQY. Meanwhile, above diameter of 12 nm, the radiative recombination rate is nearly constant, while it increases linearly below this threshold diameter, ultimately reaching a value at 5.7 nm that is 54 times higher than that at 250 nm. As the NW diameter shrinks, we also expect the non-radiative recombination rate to boost due to the increased surface recombination.⁴² Plotting the internal and external non-radiative recombination rates versus the NW surface-to-volume ratio ($2/r$) allows us to extract a consistent SRV of ~ 18 cm s^{-1} from the slope of the linear fits (Figure 4d),³⁴ which is rather low for perovskite materials.⁴³ The strong confinement of the templates-induced super-stability of QWs over NWs and thin films are also demonstrated (Figure S5).

High quality perovskite materials with superior properties and stability are promising for optoelectronic device applications such as photodetectors with tunable spectral response.^{20-22,44} However, due to the material stability issue and incompatibility with nanofabrication processes, device fabrication using individual perovskite QWs remains a challenge. Our ultra-high density ($\sim 10^{12} \text{ cm}^{-2}$) vertical QW arrays can be simply integrated with contacts to fabricate photodetectors, as shown in the inset of Fig. 5a. In such a device, the Al substrate and the layer of 100 nm transparent ITO film ($100 \text{ } \Omega/\square$) which was sputtered without further annealing process serve as the bottom and top electrodes respectively. Figure S7 shows the transmittance of 100 nm ITO thin film sputtered on glass substrate. The schematic energy band diagrams for zero, forward, and reverse biases are shown in Figure S8. Under zero bias, the photo-generated electro-hole pairs cannot be easily collected by the electrodes because of the existence of the Al_2O_3 barrier layer between the Al electrode and the QWs. However, when applying high enough bias, carriers can gain enough energy from internal field and tunnel through the barrier layer thus leading to a large tunneling current. This asymmetric contact structure leads to a Schottky junction, which can be observed in the I-V curves under dark and white halogen

light (11.2 mW cm^{-2}) illumination (Figure 5a and S9). Note that in negative bias condition, electrons are required to overcome the energy barrier $E_{b1} \sim 0.8 \text{ eV}$ between ITO fermi level and perovskite conduction band to sustain a continuous current flow. However, in the forward bias condition, electron injection energy barrier height E_{b2} between perovskite and $\text{Al}_2\text{O}_3/\text{Al}$ is much lower. Therefore, forward bias current is much higher than the reverse bias current, as shown in Figure 5a. Figure 5b characterizes the time-domain light response under -5 V bias and pulsed white light (11.2 mW cm^{-2}) for different QW arrays. The stable photocurrent drops from $\sim 140 \text{ nA}$ to $\sim 16 \text{ nA}$ when decreasing the QWs diameter from $18.8 \pm 2.2 \text{ nm}$ to $5.7 \pm 1.4 \text{ nm}$ can be attributed to the photocarrier loss via increased radiative recombination as discussed before. Namely, under the same optical and electrical condition, more photo-generated electro-hole pairs recombine with each other and hence emit the light rather than being collected by two electrodes in the smaller QWs device. In the future, the photoresponse can be further enhanced by using shorter QWs and by removing Al_2O_3 barrier layer completely.²⁰ The typical response time of the device are extracted from the I-t curve shown in Figure 5c. The photocurrent rise time (t_{rise}) of 80 ms and fall time (t_{fall}) of 140 ms are reasonably short, and can be further

improved by shortening the QW length to reduce the resistance and charge-carrier collection time and by shrinking the top electrode area to reduce the parasitic capacitance between the two electrodes. The wavelength-dependent responsivity is characterized and shown in Figure 5d, with the input optical spectrum shown in Figure S10. In this case, the 5.7 ± 1.4 nm QW array device was used for measurement, and the same -5 V bias was applied. It can be seen that the photo responsivity has a peak value of ~ 2 mA W^{-1} and suddenly drops from 1.23 mA W^{-1} to ~ 0 when the incident optical wavelength increases from 720 nm to 730 nm, which is in excellent agreement with the absorption edge and PL emission peak shown in Figure 3a.

In this work, we demonstrate intriguing quantum confinement and nanophotonic effects in perovskite QW arrays. Particularly, quantum confinement results in 56-fold enhancement in IPLQY and nanophotonic effect contributes to 2.3-fold increase in light out-coupling, when NW diameter shrinks from bulk (250 nm) to quantum confined regime (5.7 nm). Together these two effects lead to a 130-fold substantial boost in EPLQY for QWs versus bulk NWs. In addition, it is also discovered that the QWs have a low SRV of

18 cm s⁻¹ which is comparable to state-of-the-art well passivated Si, and it is a necessary enabling condition to observe the enormous PLQY improvement. The QWs have been fabricated into photodetectors to demonstrate the ease of electrical contact for optoelectronic devices. Furthermore, the photoresponse is found to be dependent on QW diameters, due to quantum confinement as well. Together with good QW stability embedded in alumina template, the fabricated QWs may find potential applications in high performance and highly integrated optoelectronics in the future.

Method

PAM fabrication: The PAMs were fabricated by using a well-known anodic anodization with low voltages. Briefly, after being cleaned with acetone and isopropyl alcohol, a high purity Al foil with around 1.5 × 2.5 cm² size was electrochemically polished in an acidic solution made from 25 vol % HClO₄ and 75 vol % CH₃CH₂OH for 2.5 min under 12.5 V at room temperature. Afterward, the first anodic anodization was carried out by immersing the Al chip into acid solution (5 vol % H₂SO₄) under different DC voltages (5 V, 10 V, 15

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3 V, and 20 V) at 10 °C for different time (24 hours, 12 hours, 5 hours, and 3 hours,
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7 respectively. Followed by the second anodization with the same condition, an acid
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10 etching (6 wt % H_3PO_4 and 1.8 wt % CrO_3) of the first anodization layer was carried out
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13 at 98 °C for 15 min. To get 100 nm thick PAM in the second anodization, it empirically
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16 took around 20 min, 10 min, 2 min, and 1 min for 5 V, 10 V, 15 V, and 20 V anodization,
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19 respectively. At the end of the second anodization (except for the 5 V one), the DC
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22 voltage source mode was directly switched to DC current source mode with current value
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25 being half of that in voltage mode, which would trigger a voltage-ramping-down process
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28 and hence thin down the barrier layer at the bottom of PAM channels. When the voltage
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31 reached 5 V, the process was terminated and the PAM chips were rinsed with deionized
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34 (DI) water and dried with compressed air for the later use.

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43 *Pb electrodeposition:* The Pb precursor was electrochemically deposited at the bottom of
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46 PAM nanochannels in aqueous electrolyte made from 1.7 g of PbCl_2 , 25 g of trisodium
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49 citrate and 100 mL deionized water. A potentiostat (Series G-300, Gamry instruments)
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52 was used to supply a sinusoidal voltage signal with 60 Hz frequency and 5 V amplitude
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for 10 s. Nanocrystalline Pb NWs would be consequently obtained at the bottom of PAM channels.

MAPbI₃ QWs growth and photodetector device fabrication: The MAPbI₃ QWs were synthesized through the reaction between Pb and MAI vapor as reported earlier.²⁰ Briefly, the PAM chip with Pb NWs deposited was placed into the face-to-face glass bottles with MAI powder inside, which helps to trap the MAI vapor and hence promotes the reaction. A tube furnace (1-inch diameter size) with Ar carrier gas was then used to heat them up to 180 °C for 5 min to completely consume Pb precursor. To guarantee all QWs having identical length, excess Pb precursor was deposited beforehand to make sure there is a layer of MAPbI₃ thin film on the top surface of PAM template, and successively a surface ion milling process and regrowth were carried out to remove the polycrystalline thin film. Specifically, in the 1 hour ion milling process, argon ions were accelerated by 100 V voltage in a vacuum of 1.4×10^{-4} torr. The angle between the ion acceleration path and the normal of the chip is 80 degree with continuous rotation of the chip during the etching. Afterward, another VSSR process with the same growth condition was carried out but

only for 30 s to repair the ion beam damaged surface. To fabricate a photodetector device, a transparent 100 nm layer of ITO was sputtered on top of substrate without further annealing process using a circle shadow mask of 0.0314 cm² area.

Single Pb NW and MAPbI₃ QW extraction: To extract a single MAPbI₃ QW out from the PAM template for TEM, a mechanical grinding and sonication process was utilized. Followed by the MAPbI₃ QWs growth, a free-standing PAM membrane with deposited Pb NWs was obtained by HgCl₂ etching.²⁰ Afterward, the membrane was mechanically grinded into fine powder, dispersed in chlorobenzene, and sonicated for 20 min, which finally would extract QWs out from the edge of broken PAM pieces and uniformly dispersed them into the solvent. The Pb NWs extraction was carried out by using the same process except for the MAPbI₃ QWs growth step.

Characterization: SEM images of PAM were characterized using a field-emission scanning electron microscopy (JEOL JSM-7800F). XRD patterns of MAPbI₃ QW arrays in PAM were obtained using Bruker D8 X-ray diffractometer. TEM images were obtained by TEM JEOL (2010) with 200 kV acceleration voltage. UV-vis absorption and PL

including spectrum and lifetime were measured using Varian Cary 500 spectrometer (Varian, USA) and Edinburgh FS5 fluorescence spectrometer, respectively. The PLQY was measured using a custom-built micro-PL instrument reported by us before with more details in the supplementary.⁴⁵ A double-exponential function was used to fit all PL decay profiles:

$$I(t) = A + B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)}, \quad (3)$$

with fitting results shown in Table S1. The average lifetime (used to calculate radiative and non-radiative recombination rates) is given by: $\tau_{ave} = \frac{\tau_1 * B_1 + \tau_2 * B_2}{B_1 + B_2}$.

The photodetector device was characterized using a HP 4156A Analyzer along with probe station (Sigatone, US) and broadband Halogen lamp as a light source.

Simulation: The time domain light out coupling efficiency simulation for MAPbI₃ NW arrays and thin film counterpart was performed using Lumerical FDTD software package. All the NW arrays and thin film were 100 nm thick. Refractive index for perovskite is $n = 2.6$, $k = 0.2$.⁴⁶ Refractive index for Al₂O₃ is using the “Al₂O₃-Palik” in the inset material

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3 database. Dipole light sources with horizontal and vertical polarizations were used to
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7 simulate the isotropic light-generation process. Source wavelength were 713nm, 732nm,
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10 740nm, 746nm, 772nm and 772 nm for 5.7 nm, 9.1 nm, 12.2 nm, 18.8 nm, 250 nm NW
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13 arrays and thin film sample. Periodic boundary conditions were applied on the x and y
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17 directions. Then the light out coupling efficiency was extrapolated by the ratio of the far-
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21 field light power over the light source power. Cross-sectional E field monitors and time
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25 monitors were added to record the E field intensity distribution and light propagation.
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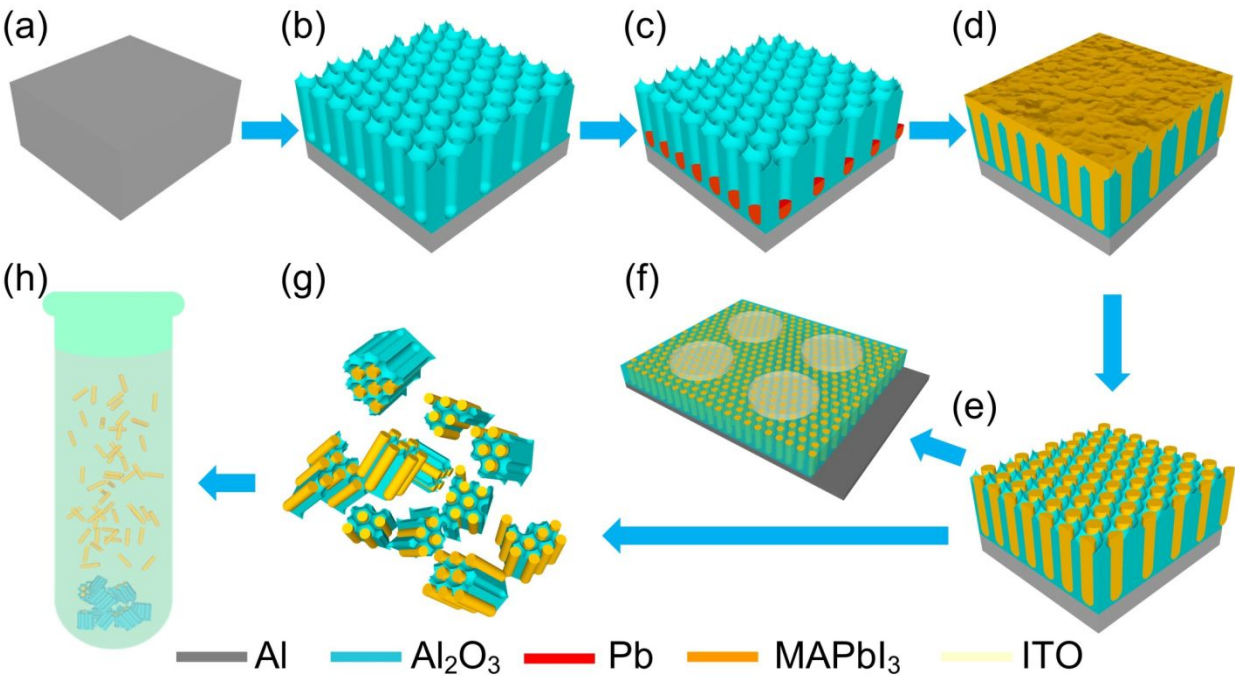


Figure 1. Schematic of PAM template assisted growth of MAPbI₃ QW arrays for single QW extraction and photodetector fabrication.

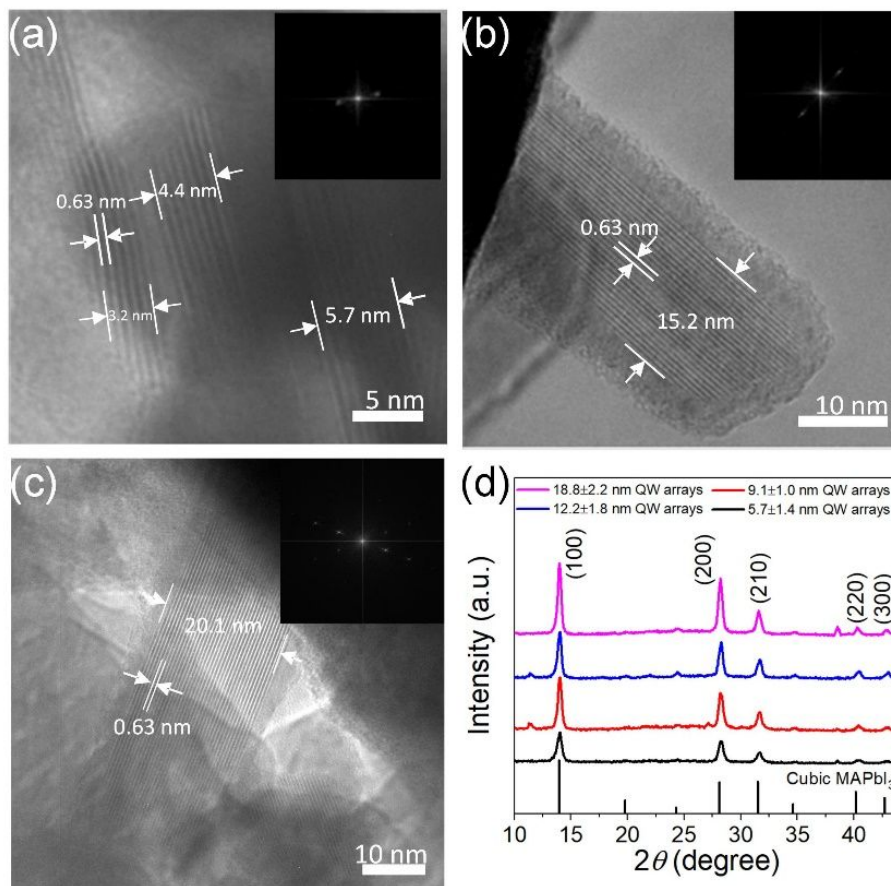


Figure 2. Crystal structure characterization of MAPbI₃ QWs. HRTEM images of MAPbI₃ QWs extracted from (a) 5 V, (b) 15 V and (c) 20 V PAM. The insets show the corresponding FFT analysis. (d) XRD patterns of MAPbI₃ QW arrays in 5 V (black curve), 10 V (red curve), 15 V (blue curve), and 20 V (pink curve) PAM, and standard cubic MAPbI₃.

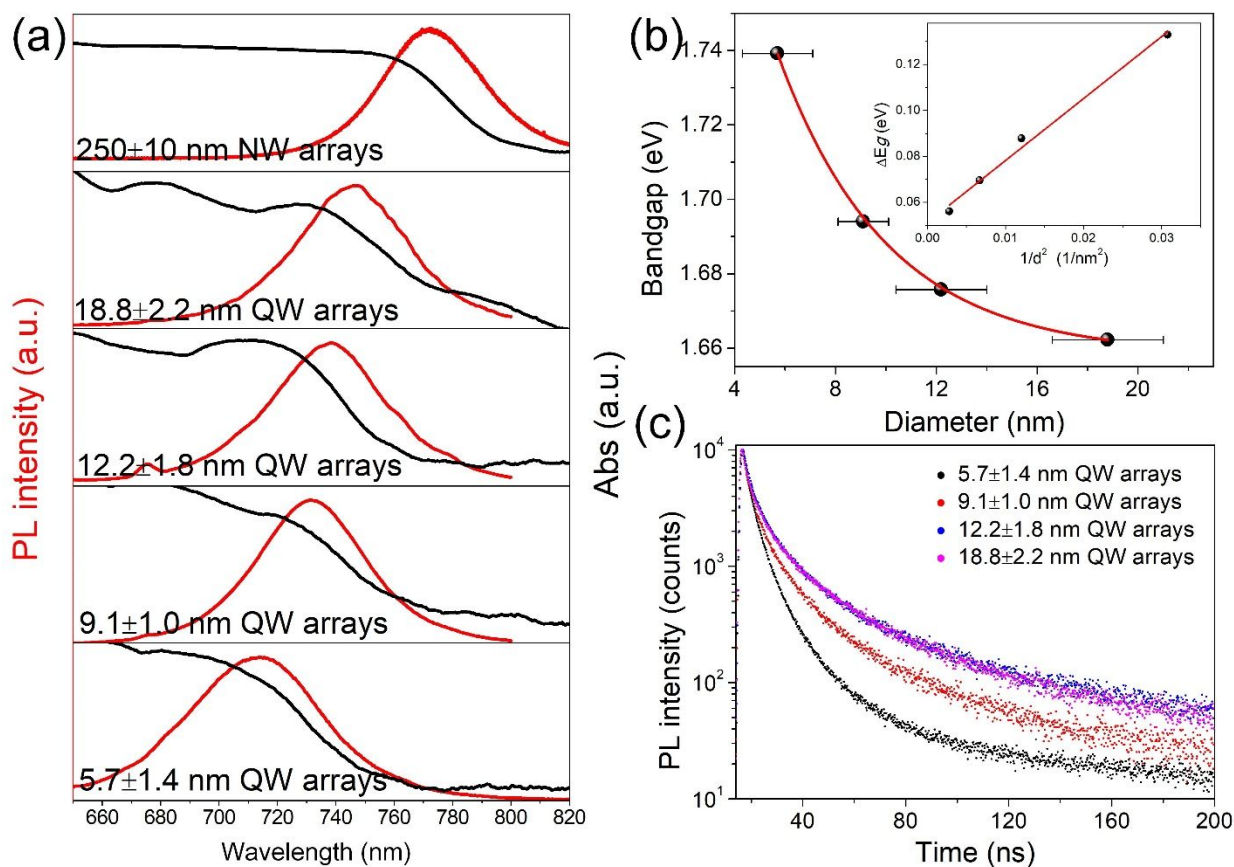


Figure 3. Optical properties characterization of MAPbI₃ QWs. (a) Normalized PL spectra ($\lambda_{\text{ex}}=400$ nm) of MAPbI₃ QW arrays in different PAM templates and MAPbI₃ NW arrays, showing a maximum 59 nm PL peak blue shift. (b) Dependence of calculated bandgap on the QW diameter. The insert: the linear fitting of bandgap change versus $1/d^2$. (c) TRPL ($\lambda_{\text{ex}}=365$ nm) measured at the PL peak for MAPbI₃ QWs with different diameters.

Table 1. Average lifetimes (τ_{ave}), light out-coupling efficiency (OCE), EPLQY and IPLQY values under $\sim 50 \text{ W cm}^{-2}$ incident power density, internal radiative (R_{rad}) and non-radiative (R_{nrad}) recombination rates for different NW arrays. τ_{ave} is extracted from the double-exponential fitting of PL decays with definition shown in Methods.

Diameter (nm)	τ_{ave} (ns)	OCE (%)	IPLQY (%)	EPLQY (%)	Internal R_{rad} ($\times 10^7 \text{ s}^{-1}$)	Internal R_{nrad} ($\times 10^8 \text{ s}^{-1}$)
5.7	4.126	90.6	42.6	45.1	3.96	2.01
9.1	6.001	89.4	13.1	14.4	1.04	1.56
12.2	8.124	72.4	0.87	1.21	0.15	1.22
18.8	8.325	56.5	0.78	1.37	0.12	1.19
250	3.039	39.8	0.33	0.81	0.19	3.1

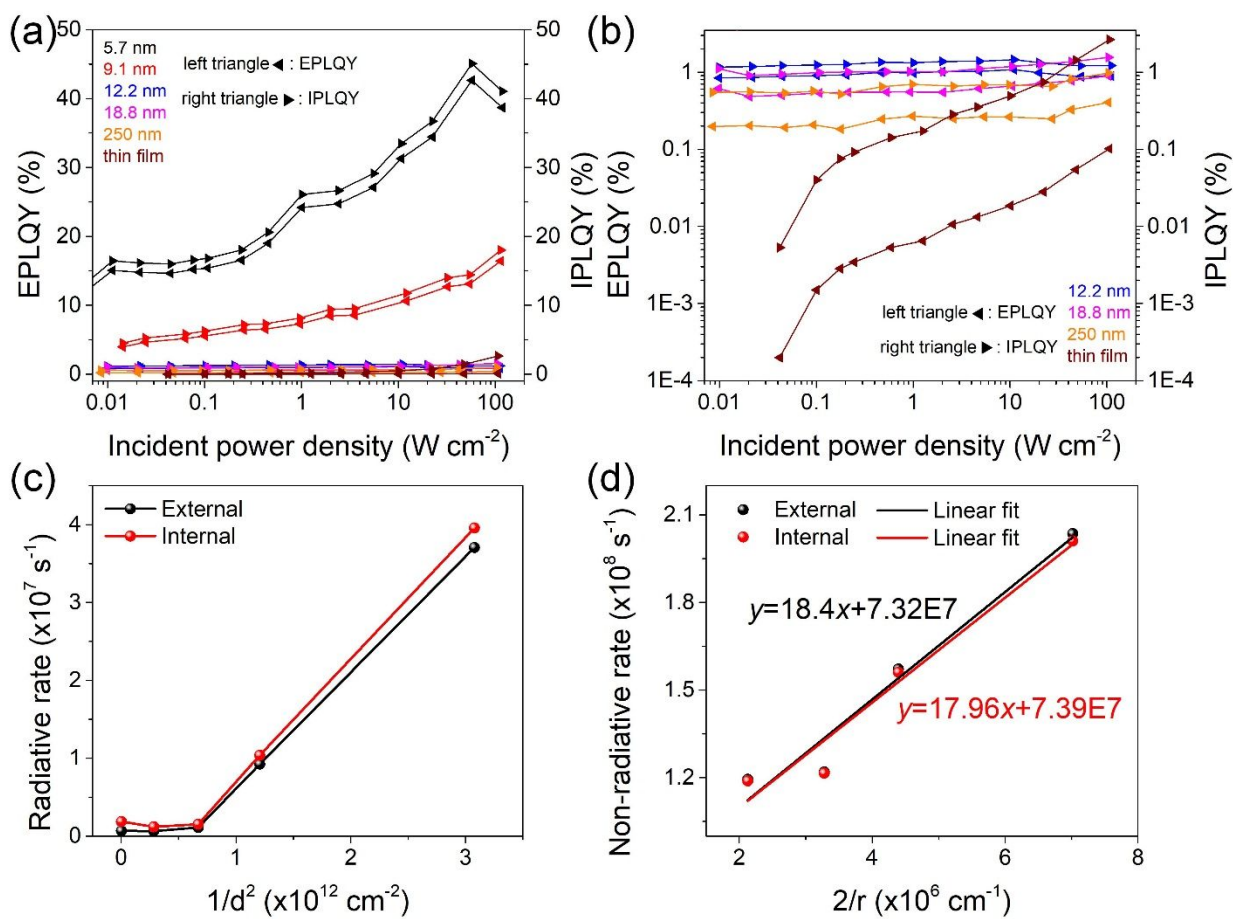


Figure 4. Optical properties characterization of MAPbI₃ QWs. Incident power density ($\lambda_{\text{ex}}=514$ nm) dependent EPLQY and IPLQY values of QW arrays, NW arrays and thin film counterpart with (a) linear scale and (b) log scale. (c) External and internal radiative

recombination rates versus the inverse NW diameter squared. (d) External and internal non-radiative recombination rate versus the nanowire surface-to-volume ratio ($2/r$).

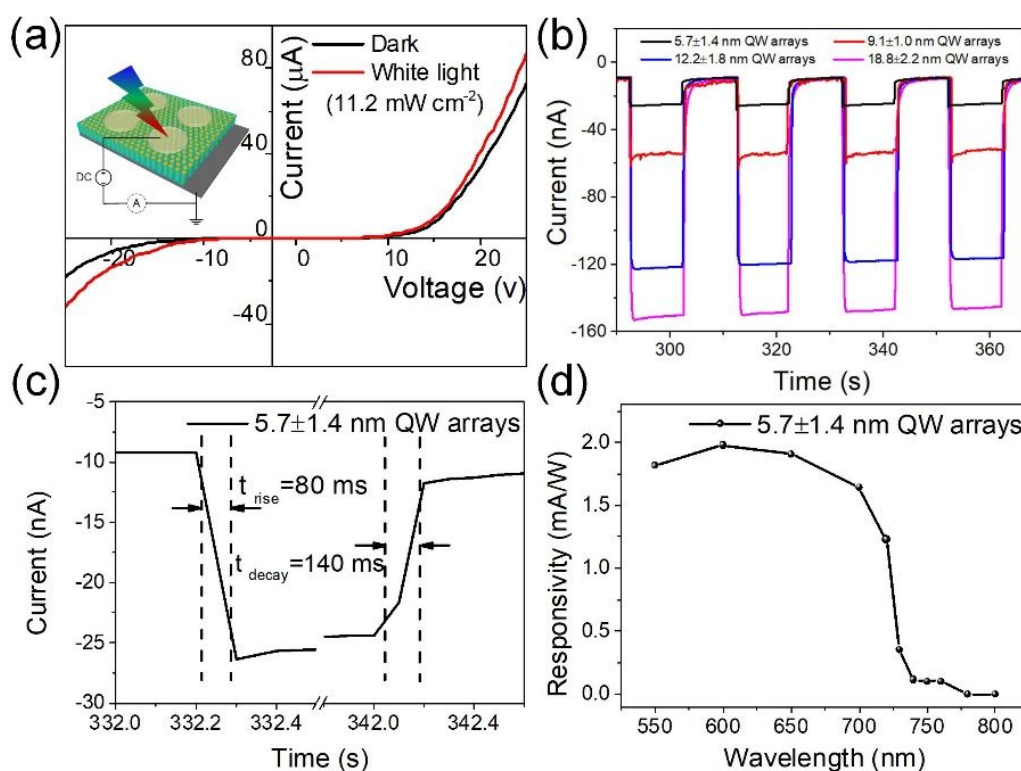


Figure 5. Optoelectronic properties characterization of MAPbI₃ QW arrays based photodetector devices. (a) I-V curves under dark condition and white color light illumination (11.2 mW cm^{-2}) for $5.7 \pm 1.4 \text{ nm}$ QW arrays based device. (b) Time-domain

photoresponses to the same white color light for different diameter MAPbI₃ QW arrays based devices under -5 V bias. (c) Response time under the same white light and (d) wavelength-dependent responsivity analysis for 5.7±1.4 nm QW arrays based device with -5 V bias.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

XXX/acs.nano letter. XXX.

AAO pore size distribution, TEM images of Pb NWs and MAPbI₃ QWs, PLQY measurement setup and method, Stability test for QWs, NWs and thin films, Dynamic QW arrays PL profiles fitting, Light out-coupling efficiency simulation, Iterative calculation of IPLQY using measured EPLQY and simulated light out-coupling efficiency, Transmittance of ITO film, Photodetector device physics and performance

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Notes

The authors declare no competing interests.

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Title: Increasing photoluminescence quantum yield by nanophotonic design of quantum-confined halide perovskite nanowire arrays

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