

Horizontally Oriented Exciton Dipoles in Solution-Processed Quantum Dot Solids

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ABSTRACT

It is well-known that the horizontally oriented exciton transition dipole moments in thin films of quantum emitters can direct radiation perpendicular to the substrate, maximizing the light outcoupling efficiency. Exciton orientation control has been reported in many thermally evaporated organic molecular thin films but has not yet been realized in solution-processed quantum dots films. Here, we demonstrate that excitons in solution-processed thin films comprised of colloidal quantum wells (CQWs) of lead trihalide perovskites are horizontally oriented, with thin-film photoluminescent quantum yields of up to 90%.

1 INTRODUCTION

Following the path of organic light emitting diodes (OLEDs), in which the external quantum efficiency (η_{ext}) has reached >40% by harvesting phosphorescence or thermally activated fluorescence [1], the semiconductor quantum dots (QDs)-based LEDs have also reached an external quantum efficiency of ~20%, reaching the theoretical limit set by the light outcoupling efficiency, η_{opt} . In order to further increase η_{ext} and minimize the radiation losses in the substrate and waveguide modes, it is required to horizontally orient exciton transition dipole moments (TDMs) in the emitter films [2]. However, excitons in quantum dot solids are much less localized as compared to those in organic molecular solids, owing to the Wannier-Mott (WM) characteristics. As a result, the interplay between inter-NC charge transfer, energy transfer, and geometry effects of individual QDs often leads to random exciton orientation in the QD solid film.

The fundamental mechanism inducing the WM characteristics in the excitons in the semiconductor QD films is the fact that the dielectric constant, ϵ , in semiconductor is intrinsically high ($\epsilon \sim 10$). Despite a high degree of quantum confinement in quantum dots, the enhancement of exciton binding energy is not sufficient to localize excitons in individual QDs. Here we show that this fundamental limitation can be overcome in the self-assembled structures of colloidal quantum wells (CQWs) [3-6] of lead trihalide perovskites. First, the two-dimensional (2D) morphology confines excitons in a plane, such that the TDMs are predominantly in-plane (IP). Second, by carefully controlling the solution deposition

process, one can stack the CQW nanocrystals in a layer-by-layer fashion with the surface normal vector perpendicular to the substrate plane. Third, unlike other traditional semiconductors, the dielectric response of perovskites is highly frequency-dependent. The exciton binding energy, which is determined by ϵ at the visible frequency ($\sim 10^{14}$ Hz) ϵ_{optic} , is high, because a low $\epsilon_{\text{optic}} \sim 4$. But the electrostatic interactions, which are determined by ϵ at low frequencies ($< 10^{12}$ Hz) ϵ_{ion} , are very small due to a very high $\epsilon_{\text{ion}} \sim 30$. Accordingly, the inter-NC interactions are minimized while the intra-QD excitons still have a high binding energy. This minimizes the coupling between QDs upon CQW assembly.

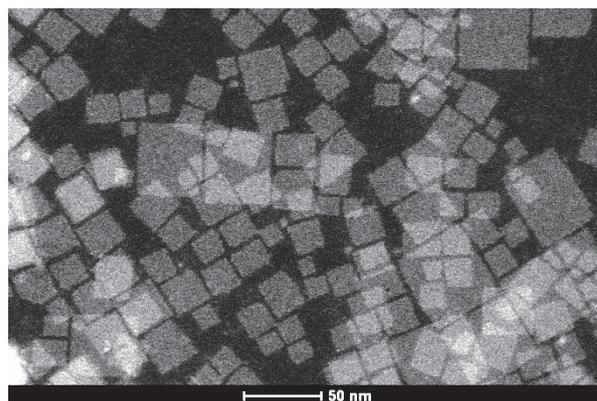


Fig. 1 Transmission electron micrograph of synthesized monodispersed CQWs with uniform thickness of 2.4 nm.

2 RESULTS

We colloiddally synthesized monodisperse CQWs with uniform thickness that can be precisely controlled from 1.8 nm to 5 nm, as shown in Fig.1. The CQWs have the photoluminescence quantum yield (η_{PL}) of 50-90%. The ligand chemistry allows us to tune the inter-QD distance from ~3 down to 0.6 nm. We carefully engineer the solution coating process such that we are able deposit superlattice films of CQWs with controllable thickness. The superlattice film was deposited on a glass substrate with its c axis perpendicular to the substrate (x - y) plane. The film thickness and the refractive index were determined by ellipsometry.

Each sample (air/superlattice/substrate; Fig. 2(a))

was attached to a hemicylindrical glass prism, followed by carrying out the polarization- and angle-dependent PL spectroscopy [2] that differentiates between the p -polarized (p -pol) emission from the transverse-magnetic (TM) x and z dipoles and the s -polarized (s -pol) emission from the transverse-electric (TE) y dipoles. The generated radiation pattern characterizes the PL intensity I on the x - y projection of emission wave vector \mathbf{k} (Fig. 1a), k_x and k_y , which reveals the dipole orientation in the superlattice within the k space domain, $k/k_0 < n_{\text{sub}}$, where k_0 is the wave vector in air and $n_{\text{sub}} = 1.52$ is the refractive index of substrate. It follows that $k/k_0 = 1$ corresponds to the critical angle of total internal reflection (TIR) at the glass/air interface. Under the assumption of uniform dipole distribution in the superlattice, optical simulations were then carried out to fit the p -pol profile, using Θ_{IP} , the probability of horizontally oriented dipole, as the only fitting parameter.

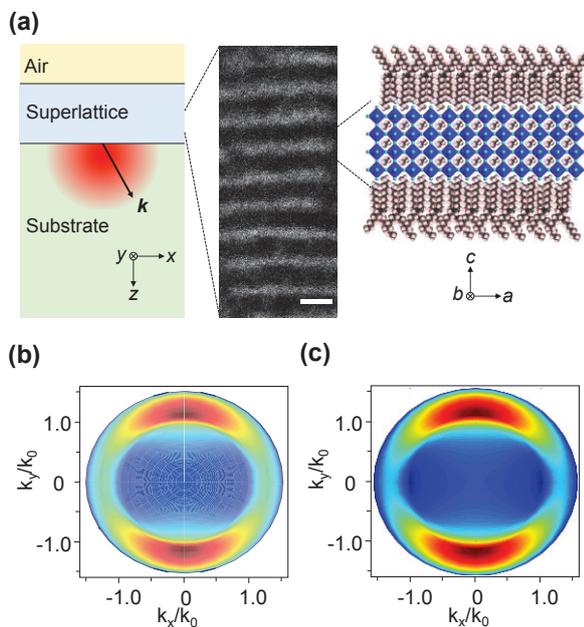


Fig. 2 (a) Schematic of the fabricated superlattice of CQWs with Miller index (a, b, c) with respect to the substrate coordinate (x, y, z). Upon optical excitation the radiation has the emission wavevector \mathbf{k} that can be characterized using the angle- and polarization-dependent spectroscopy. The radiation patterns of superlattice films comprised of CQWs with thickness of (b) 5 nm and (c) 2.4 nm, giving Θ_{IP} of 0.72 and 0.85, respectively.

Figs. 2(b) and 2(c) present the radiation patterns of two thin film samples comprised of CQWs with thicknesses of ~ 5 and 2.4 nm, respectively. The thin-film η_{PL} values are all greater than 0.8 in both samples. The radiation patterns can be nicely fitted by the optical simulations, yielding Θ_{IP} values of 0.72 and 0.85, respectively, both are considerably higher than the isotropic orientation

distribution ($\Theta_{\text{IP}} = 0.67$). As we illustrated earlier, to our knowledge, the lead trihalide perovskite CQW systems represent the only semiconductor QDs giving rise to control over the exciton transition dipole moment in their superlattices.

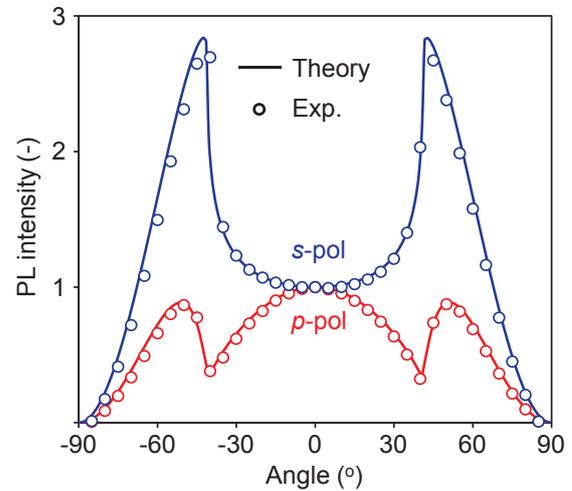


Fig. 3 Comparison between theoretical and experimental PL intensity as a function of angle for the superlattice thin film sample containing perovskite CQWs with thickness of 2.4 nm.

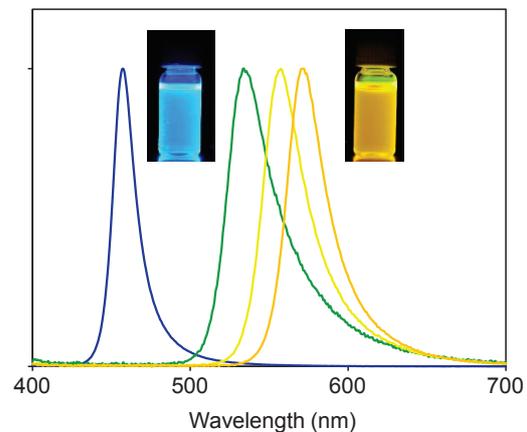


Fig. 4 Emission spectra for the as-synthesized pure-bromide (blue curve) and iodide-doped (green, yellow, and orange curves) perovskite CQW colloidal solutions. The insets show the photographs for the blue and orange samples under excitation of UV light.

Note that in OLED community, the k -space radiation pattern is less documented but it is in fact equivalent to angle-dependent PL spectra. For example, one can easily convert Fig. 2(c) to Fig. 3, by extracting p -pol ($k_x = 0$) and s -pol ($k_y = 0$) cuts as a function of angle θ . We notice that most literature did not discuss the s -pol information because it only contains IP information, but strictly speaking, the experiment-optical simulation fitting

has to be consistent in both curves so that the extracted Θ_{IP} is convincing. Fig. 3 presents both s-pol and p-pol profiles for the thin film sample containing the 2.4 nm perovskite CQWs, unambiguously demonstrating emission directionality of $\Theta_{IP} = 0.85$.

An important merit for the perovskite QDs is that one can fine tune the emission wavelength by anionic or cationic doping. This can also be performed on our perovskite CQWs as well. We developed the post-anionic exchange (AE) protocols that dope as prepared bromide CQWs with iodides, as shown in Fig. 4. We were able to prepare superlattice thin films out of these solution samples and reached the same degree of Θ_{IP} , ranging from 0.80 to 0.84.

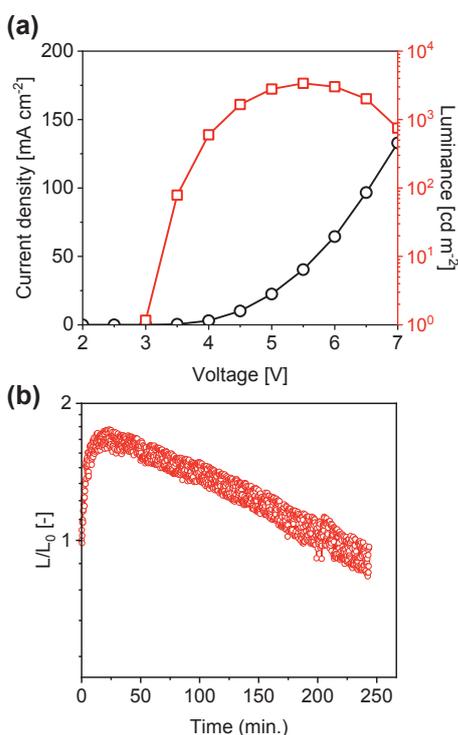


Fig. 5 Characteristics of our optimized LED devices using CQWs with thickness of ~5 nm. The maximum external quantum efficiency reaches 11.2%. (a) Current density and luminance as a function of driving voltage. (b) Normalized luminance at a constant current of 6 mA cm⁻², or an initial luminance L₀ of ~500 cd m⁻².

We fabricated LEDs using the perovskite CQWs and reached high efficiencies with the ~5 nm thickness CQWs. More efforts are required make high-efficiency LEDs with thin CQWs, because they require a high concentration of organic ligands to synthesize the compounds. As shown in Fig. 5, we reached a maximum external quantum efficiency of 11.2% and a maximum current efficiency of 36 cd A⁻¹. The device demonstrated a decent operational lifetime under a constant current of 6 mA cm⁻²,

corresponding to an initial luminance of ~500 cd m⁻². The device luminance increased and reached ~1.7 L₀ before starting to decay. The time required for the luminance decreases to 85% of L₀ is ~4 hours.

3 CONCLUSIONS

In this work, we show that in quantum dot solids, it is still possible to control the orientation of exciton transition dipole moment. By engineering the materials system and processing, it might be a promising candidate to overcome the efficiency limitation set by the light outcoupling efficiency.

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