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Plasmon Enhanced Emission of Perovskite Quantum Dot Films

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ABSTRACT

We propose and demonstrate the photoluminescence enhancement of $CsPbBr_3$ perovskite quantum dot films in the presence of Au nanoparticles. Embedded into a polymer matrix, Au nanoparticle- quantum dot film assemble prepared by an easy spin coating method enabled the photoluminescence enhancement of perovskite quantum dot films up to 78%. The properties of the synthesized perovskite QDs and gold nanoparticles have been analysed using high resolution transmission electron microscopy, X-ray diffraction, energy dispersive X- ray spectroscopy, UV-Vis absorption spectrophotometer, steady state and time-resolved photoluminescence spectrometer.

INTRODUCTION

0D nanoparticles, also known as quantum dots have been on the basis of top-notch optoelectronic devices in recent years owing their exotic optical properties. Their high quantum yield along with their tuneable optical properties based on synthesis methodologies has made them important building blocks of future electronics [1]. In recent years, apart from the mature material systems of semiconductor nanocrystals, all inorganic halide perovskite quantum dots (PQDs) have also gained great attention owing to their high photoluminescence quantum yield and very narrow emission bandwidth [2,3]. $CsPbX_3$ (X: Cl, Br, I) type perovskite quantum dots have been shown to reach up to 90% quantum yield possessing full-width half maximum values as narrow as 12 nm [2]. In that respect, their applications have started to emerge as electroluminescent materials and color converters [4-6]. Despite all the advantages PQDs offers, preserving high quantum yield in their film form still remains a challenge, which is an important limitation for device applications.

One of the mechanisms to overcome the limitation is metal enhanced fluorescence. Plasmonic nanoparticles are widely been used as light harvesting agents for applications in photovoltaics and light emitting diodes [7-11]. Based on the collective oscillations of free electrons of the metal nanoparticles, localized in optimal distances with the quantum dots, metallic nanoparticles have been shown to enhance the local electric field and increase the photoluminescence intensity of the semiconductor quantum dots [12-14]. This sort of interaction depends on the spectral overlap of the metal absorption and the fluorescence of the emitter as well as the distance between the emitter and the metal nanoparticle [15]. In that regards, although optimally spaced metal nanoparticle and emitter would enable the enhancement of the emitter, a metal nanoparticle would also quench the emission of the emitter when in contact [16]. In order to control the interparticle distance, layer by layer assembly of the spacer are commonly used in the literature for the precise plasmonic control at the nanoscale [17-19]. However, such methods are not applicable in the large scale device applications and there is a need for a technological ease in controllling the plasmonic effect. In this work, for the first time, we propose and demonstrate the enhancement of the in film photoluminescence of the perovskite quantum dots, possessing the photoluminescence enhancement up to 78%, in which the plasmonic control has been attained by changing the concentration of the metal nanoparticle in the spin coated film. High quality green emitting $CsPbBr_3$ perovskite quantum dots have been synthesized with 85% quantum yield and emission full width at half maximum of as narrow as 18 nm. Au nanoparticles synthesized in organic phase with ca. 10 nm average size (diameter) and perovskite quantum dots has been blended into polystyrene, and the control of the particle-particle distance within the spin coated film was achieved by tuning the concentrations of perovskite quantum dot-Au nanoparticles. Plasmon coupled perovskite quantum dots has been monitored further using time resolved photoluminescence spectroscopy.

EXPERIMENTAL DETAILS

Synthesis of Au and QD nanoparticles

Au nanoparticles have been synthesized using slightly modified literature recipe presented in previous literature [20]. Gold(III) chloride hydrate (1 mmol, 340 mg) and 20 mL oleylamine (OA) were loaded into a triple neck flask. Under Ar flow, $AuCl_3.H_2O$ was dissolved in OA at 60 ^{0}C for 30 min. The solution was heated to 150 ^{0}C under stirring and kept at this temperature for 2 hours. After cooling to room temperature, methanol was added to precipitate gold nanoparticles and final solution was washed with methanol to remove by-products. Obtained gold NPs were dissolved in chloroform and kept at +4 ^{0}C.

Perovskite QDs have been synthesized according to previous literature [2,21], Preparation of Cs-oleate: 0.407 g of Cs_2CO_3, 20 mL of ODE and 1.55 mL of oleic acid were loaded into a flask and dried under vacuum for 1h at 120 °C. Then mixture was heated to 150 °C under argon and used after the complete dissolution. Remaining mixture was stored under glove box.

Synthesis of $CsPbBr_3$ perovskite quantum dots: 0.19 mmol of $PbBr_2$ and 5 mL of ODE were loaded into a 25 mL flask and dried under vacuum for 1 h at 120 °C. Then 0.5 mL oleylamine and 0.5 mL oleic acid were injected to flask at 120 °C under Ar flow.

After the dissolution of $PbBr_2$, the mixture was heated to 180 °C and 0.4 mL of Cs-oleate solution was swiftly injected into the flask and 5s later, the mixture was cooled down.

For the purification of the synthesis, the mixture was loaded into a 50 mL centrifuge tube and centrifuged for 3 min at 5000 rpm and supernatant was discarded. 300 µL of hexane was added to precipitate and NCs was dispersed. Then, the solution was centrifuged again for 3 min at 5000 rpm and this time supernatant was taken. Finally, 300 µL of hexane, 25 µL of oleic acid and 25 µL of oleylamine and 600 µL of acetone was added. The mixture was centrifuged 3 min at 5000 rpm and supernatant was discarded. NCs were dissolved in fresh hexane.

Synthesized different volumes of Au NP in chloroform and perovskite QD dispersed in chloroform were mixed in 600 µL polymer solution. This mixture was spin coated on 2x2 cm^2 glass slide. The speed of the spin coater was 4000 rpm for 60 sec. and 1000 rpm for 10 sec. respectively.

Characterizations

Agilent-Cary Eclipse fluorescence spectrophotometer and UV-Vis spectroscopy Thermo Genesys 10S spectrometer have been used for PL measurements and UV-Vis spectroscopy, respectively. TCSPC measurements have been performed using Pico Quant FluoTime 200 equipped with 375nm pulsed laser diode and X-ray diffraction characterization has been performed by using PANalytical: X'pert Pro MPD. TEM images have been taken by using FEI Tecnai G2 F30 equipped with Energy Dispersive X-ray spectroscopy (EDAX), and XPS measurements have been carried out using Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer System.

RESULT AND DISCUSSION

Figure 1 presents the high-resolution transmission electron microscopy image of the $CsPbBr_3$ quantum dots (figure 1 (a)) and Au nanoparticles (figure 1(b)). The weight percentages of the $CsPbBr_3$ quantum dots extracted from EDAX measurement are 12.91%, 48.84% and 38.24% for the Cs, Pb and Br respectively.

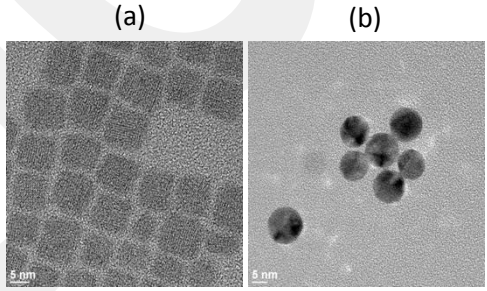

Figure 1. High resolution transmission electron microscopy image of (a) $CsPbBr_3$ quantum dots, (b) Au nanoparticles.

The absorbance and fluorescence spectra of the synthesized Au nanoparticles and $CsPbBr_3$ perovskite quantum dots in solution form respectively is presented in figure 2. Since spectral overlap of the metal absorption and the fluorescence of the emitter is critically important for the metal enhanced fluorescence, the synthesis methodology has been engineered as to couple the absorbance spectra of the metal nanoparticles with the emission peak of the perovskite quantum dots. $CsPbBr_3$ perovskite quantum dots are measured to have 85% quantum yield (as compared with Rhodamine 6G organic dye) and emission full width at half maximum value of 18 nm. The spectra in solution have not changed significantly when the film formation has been attained.

Upon achieving high quality perovskite quantum dots and Au nanoparticles, the particles have been blended in polystyrene in chloroform (%10 w/v) used as polymer matrix. Stock solutions of Au NP in chloroform and perovskite QD dispersed in chloroform were mixed in polymer solution. In order to study the effect of concentration of Au nanoparticles and perovskite quantum dots, starting with an optimal perovskite quantum dot concentration in polystyrene, Au nanoparticles have been systematically added into solution in order to observe the effect of interparticle distance in the film form. This mixture was spin coated on a glass slide. Starting with an initial 3µl of PQDs (15 mg/ml concentration in hexane), Au nanoparticles with varying the concentration from 1 µL to 10 µL (0.042 mg/ml concentration in chloroform) has been varied to generate an efficient plasmonic system in polystyrene.

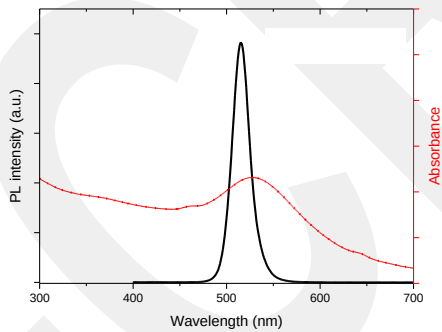

Figure 2. Absorbance spectrum of Au NP and PL spectra of perovskite QD in solution

Figure 3 presents the steady state emission spectra of the bare spin coated PQD film with changing the amount of the Au nanoparticles in the spin coated film. The steady state photoluminescence signal increases as more and more Au nanoparticles have been introduced in the film up to a certain Au nanoparticle concentration and then starts to decrease beyond certain level. This is in agreement with the previous literature that the plasmonic particle and quantum dot has to be at certain distance in order to provide a photoluminescence enhancement. However, as the interparticle distance goes beyond a certain level, the metal nanoparticle no longer provides an enhancement but a decrease in the emission of the quantum dot. In that respect, the maximum enhancement of the PQD film is achieved with 78% enhancement when 7.5 µL gold nanoparticle solution and 3 µL QD solution was incorporated in the polymer film.

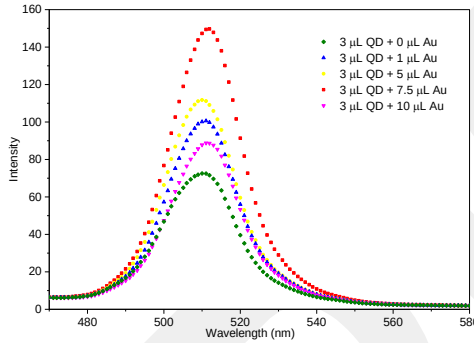

Figure 3. Steady state photoluminescence spectra of PQD films with varying the gold concentration.

In order to comment further on the origin of the plasmonic enhancement, the prepared spin coated films have further been analysed using time resolved photoluminescence spectroscopy. The time resolved photon decays of the spin coated samples is presented in figure 4. We have focused on the photon decay of the bare perovskite quantum dot with optimal amount of metal nanoparticle in the film to provide plasmonic enhancement and beyond the optimal metal nanoparticle concentration. Starting with the amplitute weighted lifetime of 5.97 ns in the bare film, the lifetime shortens to 4.91 ns in the case of 7.5 μL Au nanoparticles incorporated into the film, and the lifetime increases further to 6.20 ns when the metal nanoparticle concentration further increases to 10 μL. Table I presents the corresponding lifetimes and double exponential fit amplitudes of the lifetime values for the samples with 3 μL QD-0 μL Au spin coated film with increasing the amount of Au nanoparticles in the assembly focusing on the 7.5 μL and 10 μL of Au nanoparticle integration.

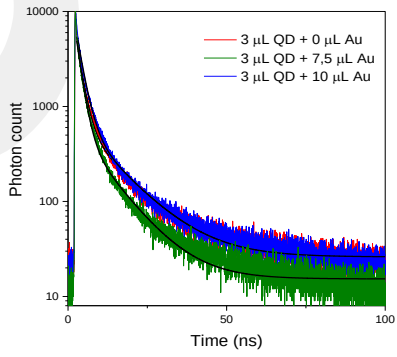

Figure 4. Time resolved photoluminescence spectra of PQD films with varying the gold concentration.

Table I Lifetime decay amplitudes and intensity weighted lifetimes for plasmonic perovskite quantum dot assembly

Sample name	**A1**	**τ1(ns)**	**A2**	**τ2(ns)**	**τ average (ns) (intensity)**	**τ average (ns) (amplitude)**
3 µL QD-0 µL Au	690±23.7	10.66±0.27	4718±141	1.69±0.05	5.97	2.83
3 µL QD-7.5µL Au	526.4±20.2	9.60±0.26	4364±120	1.68±0.04	4.91	2.53
3 µL QD-10µL Au	628.2±20.6	11.57±0.28	4620±116	2.02±0.05	6.20	3.17

CONCLUSION

In conclusion, in this work we present an investigation of the plasmonic enhancement of the perovskite quantum dot films enabled by Au nanoparticles incorporated into polymeric films, in an easy process of spin coating, which possess 78% enhancement of the fluorescence. Plasmon enhanced emission of perovskite quantum dots will open up new possibilities for future optoelectronic devices.

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