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Two-photon pumped amplified spontaneous emission based on all-inorganic perovskite nanocrystals embedded with gold nanorods

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ABSTRACT

$CsPbBr_3$ nanocrystals have attracted great interest owing to their high fluorescence quantum efficiency, adjustable photoluminescence wavelength, and good stability. We report a device that consists of disordered gold nanorods underneath a film of $CsPbBr_3$ nanocrystals. Two-photon pumping using femtosecond laser pulses at 800 nm enables amplified spontaneous emission (ASE) at about 523 nm. In this work, a narrow peak with linewidth of 5 nm is observed when the pump fluence reaches a low threshold of 0.65 mJ/cm^2. The results show that plasmonic resonance of gold nanorods improves the emission transition rate and enables low threshold ASE.

1. Introduction

A new quantum dots (QDs) system, all inorganic cesium lead halide perovskite nanocrystals (NCs) ($CsPbX_3$, X = Cl, Br, I), has aroused wide research interest in the recent decade. $CsPbX_3$ NCs have been reported with potential applications for photovoltaic and optoelectronic devices due to their excellent properties [1–5], such as high fluorescence quantum efficiency (up to 90%), adjustable fluorescence wavelength covering the entire visible spectral region through composition manipulation and size control, narrow linewidth, and high stability [6–9]. Besides these advantages in their linear properties, $CsPbX_3$ NCs holds both efficient two-photon absorption and ease of achieving population inversion [10–12], which enable them a preferred nonlinear optical material and two-photon pumped optical gain media [13–16]. Two-photon-pumped lasers are a promising strategy to achieve frequency up-conversion for situations where the condition of phase matching requirements cannot be fulfilled [17,18]. However, the threshold based on the two-photon absorption is obviously higher than that of single-photon absorption [19,20]. To reduce the threshold, Li et al. [21] introduced ZnO nanoparticles into the $CsPbBr_3$ precursor solution to improve the surface smoothness. The ASE threshold was reduced from 0.679 mJ/cm^2 to 0.569 mJ/cm^2 in comparison with the pure $CsPbBr_3$ films. An alternative method to reduce the threshold is introducing metallic nanostructures into such QDs system. This method has been widely demonstrated and accepted in the applications of random laser [22–24] and solar cells [25,26]. In random laser, localized surface plasmon resonance (LSPR) by metallic nanostructures provides high light scattering efficiency [27] and large local field enhancement factor [28], enables low-threshold random laser. In solar cells, LSPR can accelerate the radiation transition rate of the exciton and increase the efficiency. Therefore, lowering the threshold is expected through introducing metallic nanostructures into $CsPbX_3$ NCs system. To the best of our knowledge, to date, the low threshold ASE of $CsPbX_3$ NCs based on the mechanism of LSPR has not been reported. In this paper, a device that consists of disordered gold nanorods (NRs) underneath a film of $CsPbBr_3$ NCs is successfully designed. Through two-photon pumping this device using femtosecond laser at 800 nm, the ASE with a pump threshold of 0.65 mJ/cm^2 is produced.

2. Experiments

2.1. Materials

Hexadecyl trimethyl ammonium bromide (CTAB, 98%), L-ascorbic acid (> 99.7%), $HAuCl_4$ (> 47.8%), Sodium borohydride ($NaBH_4$, > 98%) and $AgNO_3$ (99.8%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all the experiments. The $CsPbBr_3$ NCs with quantum yield of 88% were purchased from Nanjing MKNANO Tech. Co., Ltd.

2.2. Synthesis of gold NRs and $CsPbBr_3$ NCs film

Gold NRs was prepared based on the seed-mediated growth method [29]. The first step is to prepare the seed solution. The CTAB solution (5 mL, 0.2 mol) was mixed with $HAuCl_4$ (5 mL, 0.5 mmol) with stirring bar for about 30 min at 60 °C. Then, ice-cold $NaBH_4$ (0.5 mL, 10 mmol)

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was added, which formed the brownish yellow solution. The seed solution was stirred for 5 min and then kept it at room temperature. The second step is the growth of gold nanorods. CTAB (5 mL, 0.2 mol) was mixed with $AgNO_3$ solution (0.25 mL, 0.004 mol) at 25 °C. $HAuCl_4$ (5 mL, 1 mmol) and ascorbic acid (70 μL, 0.0788 mol) were added successively. With strong stirring, the color of the growth solution changed from dark yellow to colorless. Finally, seed solution (12 μL) was added into the growth solution and kept it at 27–30 °C. The color of the solution gradually changed within 15 min. After 6 h growth, deionized water was used to wash the solution for three times.

The aqueous solution of gold NRs with a concentration of 15 mg/mL was drop-coated onto the silica substrate followed by a drying process at about 60 °C for 2 h. The solution of $CsPbBr_3$ NCs was then drop-coated onto the gold NRs, which was prepared by mixing the $CsPbBr_3$ NCs in chloroform with a concentration of 20 mg/mL. Thus, a $CsPbBr_3$ NCs doped waveguide was produced on top of the gold NRs structure.

2.3. Film characteristics

Scanning electron microscope (SEM) and transmission electron microscopy (TEM) images were recorded using JEOL JSM-7800 F microscope and JEM-2100 F microscope at 200 kV, respectively. The thickness of the films was characterized by profilometer (Dektak 150, Veeco, USA). Fluorescence and extinction spectra were characterized by fluorescence spectrometer (F-4600, HITACHI, Japan) and UV–Vis spectrophotometer (G1103A, Agilent Technologies, USA). The refractive index was measured with a spectroscopic ellipsometer (ESNano, Elltop Scientific Co., Ltd. China). The software of Nano measure developed by Fudan University in China was used for statistical analysis of TEM images.

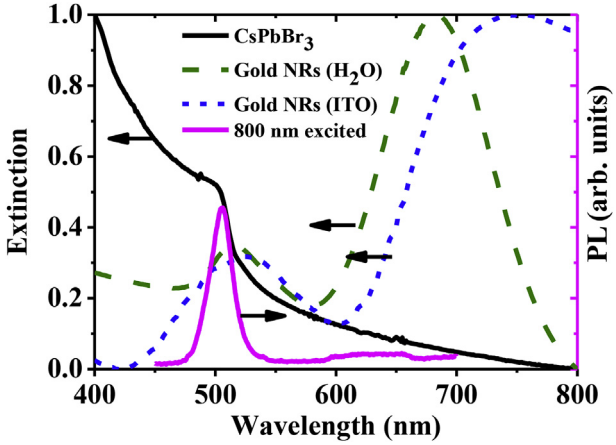

Fig. 2. The extinction of $CsPbBr_3$ NCs (in black), gold NRs in aqueous solution (in green) and on ITO (in blue). The photoluminescence spectra of $CsPbBr_3$ NCs excited by femtosecond laser with center wavelengths of 800 nm (in pink). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussions

Fig. 1(a) shows the structure diagram of the designed device. Fig. 1(b) is the SEM image of the gold NRs drop-coated on silica substrate. It can be clearly seen that the gold NRs are randomly distributed on the silica substrate. Fig. 1(c)–(e) show the TEM image and size distributions of gold NRs used for this device. The diameter and length are about 15 nm and 45 nm, respectively. Fig. 1(f) and (g) illustrates the TEM image of the $CsPbBr_3$ NCs and the size distribution is shown in

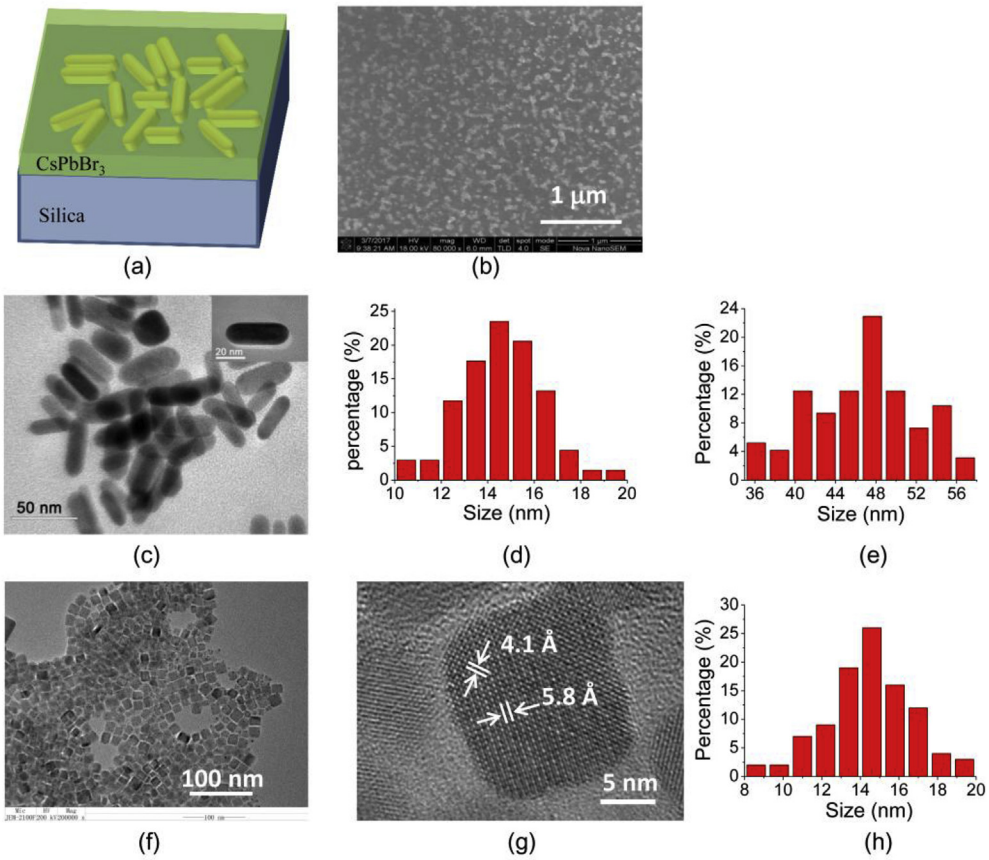

Fig. 1. (a) The structure of the experimental sample. (b) SEM image of gold NRs. (c) TEM image of gold NRs. (d) Diameter distribution of gold NRs. (e) Length distribution of gold NRs. (f) TEM image of $CsPbBr_3$ NCs. (g) High resolution TEM image of $CsPbBr_3$ NCs. (h) Size distribution of $CsPbBr_3$ NCs. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)