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Synthesis, Structure and Photoluminescence Properties of 2D Organic–Inorganic Hybrid Perovskites

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Abstract: Two-dimensional (2D) layered hybrid organic–inorganic perovskites have potential applications in solar cells, electroluminescent devices and radiation detection because of their unique optoelectronic properties. In this paper, four 2D layered hybrid organic–inorganic halide perovskites of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ were synthesized by solvent evaporation. Their crystal structure and surface morphology were studied. The effects of different halogens and organic amines on perovskites' absorption spectra were investigated, and the photoluminescence (PL) properties were studied by femtosecond ultrafast spectroscopy. The experimental results show that the four perovskites are well crystallized and oriented. With the increase of halogen atom number (Cl, Br, I) in turn, the UV-Vis absorption spectra peaks of perovskites redshift due to the increasing of the layer spacing, but organic amines have little effect on the spectra of perovskites. The PL intensity increases with increasing laser power, but the lifetime decreases with increasing laser power, which is mainly due to the non-geminate recombination. This research is of great significance for realizing the spectral regulation of organic–inorganic hybrid perovskites and promoting their application in nano-photonics and optoelectronic devices.

Keywords: two-dimensional (2D) layered hybrid organic-inorganic perovskites; UV-Vis absorption spectrum; photoluminescence lifetime

1. Introduction

Two-dimensional layered organic–inorganic hybrid perovskites have received wide attention recently as the most competitive candidate in the photovoltaic field [1–3]. The general chemical formula of the perovskite is ABX_3 , in which A-sites are the organic ammonium cations, B-sites are the metal cations, and X-sites are the halide anions. The B-site cations and X-sites anions form $[\text{BX}_6]$ octahedrons by ionic interaction, which corner-share to constitute three-dimensional frameworks. The A-site cations are located in the framework cavity [4–6]. In contrast to the conventional 3D hybrid halide perovskites, the 2D layered A_2BX_4 crystal consists of the inorganic layers of $[\text{BX}_6]^{2-}$ octahedra sandwiched between interdigitating bilayers of intercalated organic ammonium cations. Generally, the A cation does not directly play a major role in determining the band structure, but its size is important. A larger or smaller A cation can cause the whole lattice to expand or contract, and subsequently change the band

structure [7]. The inorganic component offers the opportunities for high carrier mobility and a wide range of bandgap [8,9]. The organic component provides the possibility of structural diversity, highly efficient luminescence and plastic mechanical properties [10]. Importantly, these 2D layered perovskite crystals have a direct bandgap [11] with a high density of state (DOS) contributed by Pb orbitals, and thus exhibit strong light-matter interaction. In this regard, the ultrathin 2D layered perovskite crystals have shown rich optical properties, such as luminescent deep blue emission [12], exciton effect and high absorption [13]. In addition, compared with traditional polycrystalline perovskite film, 2D single-crystal perovskite promises dramatically reduced defects and notably enhanced carrier diffusion length [14]. Consequently, the improved optical and electrical properties guarantee the potential of such a new family of solution-processed semiconductors in nanoscale optoelectronic devices. An organic layer with a large energy band gap is equivalent to a potential barrier. The organic layer and inorganic layer are arranged alternately to form a multi-quantum well structure. The excitons in the inorganic layer display special optical properties, such as nonlinear absorption [15] and excitonic emission [16]. The strong exciton peaks in the optical spectra are attributed to the large exciton binding energy at room temperature [17]. Organic–inorganic hybrid perovskites have great potential applications in solar cells [18–20], electroluminescent devices [21,22], nanolasers [23–25], and photodetections [26,27].

In 2009, Miyasaka et al. initially studied solar cells with the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, yielding a power conversion efficiency (PCE) of only 3.81% [28]. In 2012, Kawano et al. studied the optical properties of the perovskite $(\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3)_2\text{PbBr}_x\text{I}_{4-x}$ [29], and found that the near-resonant transition energies between Wannier and Frenkel excitons increases with an enhancement of iodine. In 2015, Slavney et al. synthesized double perovskite structure compound $\text{Cs}_2\text{AgBiBr}_6$ [30]. It was significantly more heat- and moisture-stable compared to the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ and displayed a long carrier recombination lifetime. In 2017, Hu et al. studied the perovskite CsPbBr_3 nanoplate electroluminescence devices, which displayed a narrow PL peak centered at 530 nm with a narrow full width at half-maximum of 22 nm [31]. In 2017, Chen et al. prepared the perovskite $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ by ternary solvent method and studied the effect of the crystallization temperature and solvent volume ratio on its morphology [32]. In 2018, Luo et al. studied the solar cells with the inverted planar Hetero junction perovskites, yielding a PCE of 21% due to the elimination of nonradiative charge-carrier recombination [33].

The different properties of organic and inorganic components are united in an independent composite. The inorganic component provides the opportunities for high carrier mobility and a wide range of bandgap. The organic component offers the possibility of structural diversity and high PL quantum yield. Moreover, these properties can be easily modified by changing the organic ammonium, metal or halide [34]. Currently, perovskites have been widely studied in the field of solar cells and light-emitting diodes. However, it is rare to study the PL properties of perovskites using two-photon excitation, especially to regulate its spectral properties by changing halogens in organic–inorganic hybrid perovskites. In this paper, four kinds of perovskites— $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ —were synthesized by solvent evaporation. The laser power effect on the PL intensity and lifetime was investigated with femtosecond laser via two-photon excitation. The results show that the PL properties of perovskite can be regulated in a certain range. Using this technology to change the luminescence peak can promote the application of nano-photonics and optoelectronic devices, and promote the development of near-infrared band nano-lasers, which can be better used in optical fiber communication.

2. Experiment

2.1. Synthesis of Organic Ammonium Salts

Firstly, a certain volume of the organic amine, benzylamine (0.84 mL, 10 mmol) or n-butylamine (1.11 mL, 10 mmol), was added into anhydrous ethanol (10 mL) in a 50 mL breaker at room temperature. Secondly, the haloid acid, hydrochloric acid (1.14 mL, 10 mmol, 38 wt%), hydrobromide acid (1.36 mL, 10 mmol, 40 wt%) or hydroiodic acid (1.62 mL, 10 mmol, 45 wt%) was dropwise added into the breaker.

Then, the mixtures were heated to 50 °C and stirred for half an hour by heating magnetic stirrer and then cooled at room temperature after the mixtures had been fully reacted. Subsequently, a crude oil-like product was obtained by evaporating the solvent in a rotatory evaporator at 60 °C. The crude product (the halide amine salt) was washed by stirring for 30 min with a certain volume of anhydrous ethanol, which was repeated three times, and then finally dried at 60 °C in a vacuum oven for 24 h. The obtained organic ammonium salt was stored in an airtight container for later use.

2.2. Synthesis of Perovskite Crystals

The organic ammonium salts and PbX_2 were dissolved in *N,N*-dimethylformamide (DMF) in a molar ratio of 2:1, respectively. The mixtures were heated at 50 °C and stirred for 1 h, then the perovskites were prepared by solvent evaporation. The products were evaporated after washing with ethanol. Figure 1 shows the flow chart of synthesis of organic–inorganic hybrid perovskite crystals.

Figure 1. The flow chart of the synthesis of organic–inorganic hybrid perovskite crystals.

2.3. Synthesis of Perovskitenanosheet

The perovskite crystals were ground into powders in a mortar. The samples of a certain quality were put into a mortar and ground repeatedly to form powder with uniform particle size. The powder was transferred to a glass bottle and a certain volume of hydrous ethanol was added. The glass bottle was placed into an ultrasonic cleaner (the power was set at 100 mW and the time was set at 20 min). After the end of ultrasonic oscillation, a certain volume of solution was sucked into another glass bottle with a rubber head dropper, and the glass bottle was placed into a low-speed centrifuge (the rotation speed was set at 5000 r/min and the time was set at 5 min). After centrifugation, a certain volume of supernatant liquor was added to clean silicon slice. After drying at room temperature, perovskite nanoparticles were obtained and stored in a sealed container with constant temperature and humidity. The chemical reaction equations during the experiment are shown as follows:

2.4. Characterization

The crystal structure of the sample was analyzed by X-ray diffraction (Bruker AXS, D8 Advance, Germany). The working voltage was 40 kV, the current was 40 mA, and the scanning speed was 0.02 °/s. The surface morphology and electron diffraction of the sample were observed by transmission electron microscope (JEOL, JEM-2000, Japan), and the working voltage was 200 kV. The absorption spectrum of the sample was measured by the UV-Visible spectrometer (PerkinElmer, Lambda 35, America), and the scanning range was 200–800 nm. The PL spectrum of the sample was measured by F-380 fluorescence spectrometer. The radiation source was the He–Cd laser, the excitation wavelength was 325 nm, and the spectral measurement range was 300–800 nm.

2.5. The Experimental Optical Path

In this study, femtosecond pulsed titanium sapphire laser (Vitora) and time correlation single photon counter (TCSPC) were used to study the two-photon PL spectrum and PL lifetime of samples. The central wavelength was 800 nm, the pulse width was 8 fs, and the repetition frequency was 80 MHz. PL spectra of samples were recorded by spectrometer and PL lifetime of samples was measured by TCSPC. Experimental tests are usually carried out in dark rooms at room temperature, which can minimize experimental errors caused by natural light. Figure 2 shows the optical path of the photoluminescence test system used in the experiment, in which A1 and A2 are half wave plates, B is the polarizer, C1 and C2 are 750 nm low pass filters, M1–M7 and M9–M11 are reflectors, M8 is a reflex, O1 and O2 are objectives (the numerical aperture was 0.65), and CCD is a charge couple device.

Figure 2. The experiment optical path of photoluminescence test system.

The experimental results can be fitted to a biexponential decay function:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (5)$$

where τ_1 and τ_2 are the radiative and nonradiative decay lifetime, respectively.

3. Results and Discussion

3.1. Structure Characterization

Figure 3a,c,e,g shows crystal structures of $(C_6H_5CH_2NH_3)_2PbCl_4$, $(C_6H_5CH_2NH_3)_2PbBr_4$, $(C_6H_5CH_2NH_3)_2PbI_4$ and $(C_4H_9NH_3)_2PbBr_4$, respectively. It can be observed that the four perovskites exhibit two-dimensional layered structures. $[PbX_6]$ octahedrons are connected by common vertices, and organic amine cation is evenly filled on both sides of the octahedron in opposite ways. The molecular layers of $(C_6H_5CH_2NH_3)_2PbCl_4$ and $(C_6H_5CH_2NH_3)_2PbBr_4$ stack along the axis. The molecular layers of $(C_6H_5CH_2NH_3)_2PbI_4$ stack along the b axis. The molecular layers of $(C_4H_9NH_3)_2PbBr_4$ stack along the c axis. The organic amine cation of $(C_6H_5CH_2NH_3)_2PbBr_4$ showed disorder and occupied two equivalent positions. The organic amine cation of $(C_6H_5CH_2NH_3)_2PbCl_4$, $(C_6H_5CH_2NH_3)_2PbI_4$ and $(C_4H_9NH_3)_2PbBr_4$ showed order and occupied an equivalent position.

Figure 3b,d,f,h shows the basic unit structure of $(C_6H_5CH_2NH_3)_2PbCl_4$, $(C_6H_5CH_2NH_3)_2PbBr_4$, $(C_6H_5CH_2NH_3)_2PbI_4$ and $(C_4H_9NH_3)_2PbBr_4$. The bond lengths are given in Table 1.

Figure 3. (a) The crystal structure diagram and (b) the basic unit structure diagram of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$; (c) the crystal structure diagram and (d) the basic unit structure diagram of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$; (e) the crystal structure diagram and (f) the basic unit structure diagram of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$; (g) the crystal structure diagram and (h) the basic unit structure diagram of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$. The hydrogen linked to the carbon atom is omitted.

Table 1. Length of four samples.

	Unit: nm			
	$(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$	$(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$	$(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$	$(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$
C1–C2	0.1463	0.1494	0.1481	0.1429
C2–C3	0.1392	0.1385	0.1363	0.1482
C3–C4	0.135	0.1386	0.1372	0.1438
C4–C5	0.1369	0.1384	0.1342	0.1461
C5–C6	0.1322	0.1389	0.134	-
C6–C7	0.1412	0.1387	0.1358	-
C7–C2	0.1371	0.1387	0.1367	-
C1–N	0.1521	0.1447	0.1507	-
Pb–X1	0.2877	0.2998	0.3224	0.3005
Pb–X2	0.2841	0.2979	0.3203	0.2938
Pb–X3	0.2886	0.2982	0.3198	0.2973

Figure 4a–d shows X-ray powder diffraction patterns of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$, respectively. The diffraction peaks of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$ powder appear at 6.52° , 10.52° , 15.80° , 21.12° , 26.49° , 31.92° and 37.42° ; these diffraction peaks correspond to the crystal surface of the vertical a axis in (200), (400), (600), (800), (1000), (1200) and (1400). The diffraction peaks of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ powder appear at 6.41° , 10.63° , 15.96° , 21.32° , 26.72° , 32.18° and 37.73° . These diffraction peaks correspond to the crystal surface of the vertical a axis in (200), (400), (600), (800), (1000), (1200) and (1400). The diffraction peaks of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ powder appear at 6.14° , 12.29° , 18.48° , 24.73° , 31.05° and 37.47° . These diffraction peaks correspond to the crystal surface of the vertical b axis in (020), (040), (060), (080), (0100) and (0120). The diffraction peaks of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ powder appear at 6.42° , 12.85° , 19.33° , 25.87° and 32.50° . These diffraction peaks correspond to the crystal surface of the vertical c axis in (002), (004), (006), (008), (0010) and (0012).

The X-ray powder diffraction results show that the four perovskites with sharp diffraction peaks have very high crystallinity. As shown in Figure 4a, the diffraction peaks of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$

are parallel to the bc plane ($X00$, $X = 2, 4, 6, \dots$), indicating that the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$ has a strong preferential orientation, and the organic component and inorganic component grow and extend alternately in the bc plane to form a two-dimensional structure of the vertical a axis. As shown in Figure 4b, the diffraction peaks of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ are parallel to the bc plane ($X00$, $X = 2, 4, 6, \dots$), indicating that the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ has a strong preferential orientation, and the organic component and inorganic component grow and extend alternately in the bc plane to form a two-dimensional structure of the vertical a axis. As shown in Figure 4c, the diffraction peaks of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ are parallel to the ac plane ($0X0$, $X = 2, 4, 6, \dots$), indicating that the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ has a strong preferential orientation, and the organic component and inorganic component grow and extend alternately in the ac plane to form a two-dimensional structure of the vertical b axis. As shown in Figure 4d, the diffraction peaks of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ are parallel to the ab plane ($00X$, $X = 2, 4, 6, \dots$), indicating that the $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ has a strong preferential orientation, and the organic part is parallel to the inorganic part and extends in the ab plane. The organic component and inorganic component grow and extend alternately in the ab plane to form a two-dimensional structure of the vertical c axis [32,35].

Figure 4. The X-ray powder diffraction patterns (experimental view and theoretical view) of (a) $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$ (green), (b) $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ (black), (c) $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ (blue) and (d) $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ (red).

The thickness of the single layer in the molecular structure of perovskite is the length of one layer $[\text{PbX}_6]$ of octahedron plus two layers of organic amine cation. The interlayer spacing of perovskite molecules can be calculated by Bragg formula:

$$2d \sin \theta = k\lambda \quad (6)$$

where d is the interlayer spacing, θ is the diffraction degree, k is the diffraction class, and λ is the wavelength of X-ray. The interlayer spacing of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ are 1.35 nm, 1.44 nm, 1.68 nm and 1.376 nm, respectively.

The results show that the layer spacing of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, and $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ increases successively. This is because the atomic radius of chlorine, bromine and iodine increases successively, and the volume of crystal cells of the three kinds of perovskite also increases correspondingly, and the organic parts and inorganic metal parts of the three kinds of perovskite molecules are the same, so their layer spacing shows a trend of increasing successively. Crystal data of the four kinds of perovskites are shown in Table 2.

Table 2. Crystal data of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$.

Formula	$(\text{C}_7\text{H}_{10}\text{N})_2\text{PbCl}_4$	$(\text{C}_7\text{H}_{10}\text{N})_2\text{PbBr}_4$	$(\text{C}_7\text{H}_{10}\text{N})_2\text{PbI}_4$	$(\text{C}_4\text{H}_{12}\text{N})_2\text{PbBr}_4$
Weight	565	743	931	675
Temperature (K)	293	293	293	323
Crystal system	orthorhombic	Orthorhombic	orthorhombic	orthorhombic
Space group	Cmc2 ₁	Cmca	Pbca	Pbca
a (Å)	33.619	33.394	8.689	8.22
b (Å)	7.819	8.153	28.78	8.33
c (Å)	7.728	8.131	9.162	27.62
V (Å ³)	2034	2214	2291	1895
Z	4	4	4	4
ρ (g/cm ³)	1.846	2.230	2.699	2.370
μ (mm ^{−1})	8.814	14.836	17.34	17.30

3.2. Morphology Characterization

Figure 5 shows the bright field TEM (Transmission Electron Microscope) images, HR-TEM (High Resolution Transmission Electron Microscope) images and SAED (selected area electron diffraction) pattern of the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ nanosheets. The TEM shows different shapes and different sizes of perovskite nanosheets, which correspond to different thicker perovskite nanosheets. The local size of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$ is 800 nm. The lattice spacing is 0.261 nm with the growth direction along [100], indicating the orthorhombic phase space group Cmc2₁. The local size of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ is 600 nm. The lattice spacing is 0.294 nm with the growth direction along [100], indicating the orthorhombic phase space group Cmca. The local size of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ is 1000 nm. The lattice spacing is 0.357 nm with the growth direction along [010], indicating the orthorhombic phase space group Pbca. The local size of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ is 1600 nm. The lattice spacing is 0.263 nm with the growth direction along [001], indicating the orthorhombic phase space group Pbca.

Figure 5. (a) The bright field TEM images, (b) HR-TEM images and (c) SAED pattern of the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$ nanosheets; (d) the bright field TEM images, (e) HR-TEM images and (f) SAED pattern of the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ nanosheets; (g) the bright field TEM images, (h) HR-TEM images and (i) SAED pattern of the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ nanosheets; (j) the bright field TEM images, (k) HR-TEM images and (l) SAED pattern of the perovskite $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ nanosheets.

3.3. Absorption Spectrum

Figure 6 shows the UV-Vis absorption spectra of the perovskites $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$. The absorption peaks are located at 346 nm (3.47 eV), 392 nm (3.16 eV), 516 nm (2.33 eV) and 416 nm (2.96 eV), respectively. It can be seen that the absorption spectra of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ and $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ have a redshift. When the organic part remains unchanged, the absorption peak of the inorganic part increases, with the atomic radius of chlorine, bromine and iodine increasing in turn. As the atomic radius of chlorine, bromine and iodine increases in turn, the framework of PbX_2 in the inorganic layer increases in turn, and the band gap of PbCl_2 , PbBr_2 and PbI_2 in the inorganic part decreases in turn, resulting in the decrease of exciton binding energy in turn, so the exciton absorption peak shifts red. Therefore, the absorption spectrum of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ and $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ show redshift [36].

Figure 6. The UV-Vis absorption spectrum of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$ (black curve), $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ (red curve), $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ (blue curve) and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ (pink curve).

The absorption peaks of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ also show a redshift in Figure 6. For $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ with the same inorganic layer PbBr_2 , it can be found that the forbidden band width of perovskite samples increases with the increase of the carbon chain length. We know that organic components have little contribution to this energy band. The valence band top and conduction band bottom of perovskite generally come from atomic orbitals in inorganic components. It shows that the organic components contribute little to this energy band, and that the valence band tops and conduction band bottoms of perovskites generally come from atomic orbitals in inorganic components. However, because the short chain has a stronger push electron effect than the long chain, the charge distribution between the inorganic and organic components changes, leading to the hydrogen bond interaction between the organic and inorganic layers changes. When the length of the carbon chain is shorter, the effect of the electron effect is strong, making the positive charge on the middle metal ion smaller, further increasing the strength of the hydrogen bond. The microstructure of the inorganic layer is changed due to the influence of the hydrogen bond, and the forbidden bandwidth is also adjusted. Therefore, organic components mainly affect the band gap through the hydrogen bond. Therefore, the absorption peak of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ with a short carbon chain is higher than that of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ [37].

3.4. The Laser Power Effect on the PL Intensity

Figure 7a,c,e shows the bright field and dark field optical microscope images of the perovskites $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$, respectively. All of the perovskites present transparent crystals with regular geometric shapes. $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ emit blue photoluminescence under the femtosecond laser, while $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ emit green photoluminescence. Figure 7b,d,f shows the PL spectrum of the perovskites $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$. PL peaks are located at 415 nm (2.98 eV), 540 nm (2.30 eV) and 427 nm (2.81 eV), respectively. When the laser power increases from 10 mW to 100 mW, the PL intensity of the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ increases from 117 to 2195 photon counts; the PL intensity of the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ increases from 158 to 2771 photon counts; and the PL intensity of the perovskite $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ increases from 2320 to 13,224 photon counts.

Figure 7. (a) The optical microscope images and (b) the two-photon PL spectrum of the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$; (c) the optical microscope images and (d) the two-photon PL spectrum of the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$; (e) The optical microscope images and (f) the two-photon PL spectrum of the perovskite $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$.

It can be seen that the photoluminescence intensity increases with the increase of laser power. Because the interaction between photons and perovskite molecules is strengthened with the increase of light intensity, a large number of electrons and holes will be generated inside the perovskite molecules. The recombination of electrons and holes will release the excess energy in the form of photoluminescence, so the photoluminescence intensity increases with the increase of laser power [38].

It was found that $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ and $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ had a significant difference in the strongest PL peak, and a longer PL wavelength with a higher halogen atomic number. The band gap of PbBr_2 is larger than that of PbI_2 in the inorganic part, resulting in the increase of exciton binding energy of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$. Therefore, the PL spectrum of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ and $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ show a redshift. We can see that the PL spectrum of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ have two peaks. The lower peak is the photonic exciton generated by the inorganic layer. Binding exciton produces binding energy and emits photons with Coulomb forces after electron hole pair transition of excitons in perovskite. Therefore, the low peak is thought to be generated by the radiation excitation of excitons. At the higher peak, it can be found that compared with the front exciton emission peak, the peak width of the peak is very wide, and the energy of the luminescent peak is smaller than that of the front exciton emission peak. The existence of the peak is attributed to the luminescence caused by crystal defects. In the actual crystal, due to the arrangement of the crystal itself, the point defect, line defect and plane defect will appear in the crystal, which will affect the photoluminescence of the substance itself, resulting in higher defect luminescence peak.

3.5. The Laser Power Effect on the PL Lifetime

Figure 8a–c shows the lifetime of the two-photon PL emission (pumped at 800 nm) from the perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$. When the laser power increases from 10 mW to 100 mW, the PL lifetime of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ decreases from 0.75 ns to 0.50 ns, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ decreases from 0.67 ns to 0.46 ns, and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ decreases from 3.02 ns to 2.29 ns.

Figure 8. The PL lifetime profile of the perovskite (a) $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, (b) $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and (c) $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$.

It can be seen that the PL lifetime of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ is longer than that of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ at the same laser power. This is because the atomic radius of Br and I increases in turn, which makes the framework of PbX_2 in the inorganic layer increase in turn, and the forbidden bandwidth of PbBr_2 and PbI_2 in the inorganic part decrease in turn, resulting in the decrease of exciton binding energy. Therefore, the excitons of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ are easier to separate and emit compound fluorescence. Thus, the PL lifetime of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ is longer than that of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ at the same laser power.

It also can be seen that the PL lifetime of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ is longer than that of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ at the same laser power. The organic amine cation of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ shows disorder, which leads to greater thermal vibration and more electron scattering phonons, leading to non-radiation transition and a sharp decrease of its PL life. Therefore, the PL lifetime of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ is less than that of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ at the same laser power.

The relationship of PL intensity and lifetime with laser power can be explained with the energy level diagram [39–42], as shown in Figure 9. Under the excitation of 800 nm femtosecond laser, the perovskite molecules absorb two photons, exciting the electrons at the top of the valence band to the bottom of the conduction band. Some electrons from the bottom of the conduction band will go back to the top of the valence band, releasing the excess energy in the form of photoluminescence. The electrons at the bottom of the conduction band also relax to the defect state on the electron surface and then return to the top of the valence band and compound photoluminescence with the defect state. The emission intensity is related to the absorption cross section of two photons. As the laser power continues to increase, more and more electrons are excited to the bottom of the conduction band. Some of the electrons at the bottom of the conduction band return to the top of the valence band, and another part relaxes to the defect state of the electron surface and then returns to the top of the valence band. In this process, carrier density increases and the non-geminate recombination plays a dominant role. Therefore, the two-photon PL intensity increases with the increase of laser power, while the PL lifetime decreases with the increase of laser power [43].

Figure 9. Energy level schemes of the perovskites. VB, valence band; CB, conduction band; ESSs, electron surface defect states; relaxation, the relaxation process; emission, emission process; $h\nu$, the energy of a single photon.

4. Conclusions

Four organic–inorganic hybrid perovskites of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ were successfully prepared by solvent evaporation. The crystal structure, surface morphology and optical properties of perovskites materials were studied by X-ray diffraction, transmission electron microscopy, fluorescence spectrophotometer, ultraviolet-visible spectrophotometer and optical confocal microscopy. The effects of different halogens and organic amines on perovskite absorption spectra and PL spectra were investigated. The experimental results show that under the same conditions of organic amines, with the increase of halogen atomic number, halogen radius and corresponding perovskite cell volume increase, perovskite interlayer spacing shows a trend of increasing in turn; the framework of inorganic layer PbX_2 increases in turn, and the forbidden bandwidth of inorganic layer PbX_2 decreases in turn, resulting in the decrease of the exciton binding energy. The binding energy decreases in turn, the peak value of UV-Vis absorption spectra appears to redshift, and the PL lifetime decreases in turn. Under the same inorganic layer, different organic amines will distort the inorganic framework and affect the luminescence properties of perovskite, but organic amines have little effect on the exciton luminescence of perovskites. With the increase of laser power, the two-photon PL intensity of perovskite increases with the increase of laser power, while the PL lifetime decreases with the increase of laser power, mainly the non-geminate recombination. With the development of research on organic–inorganic hybrid perovskite materials, we can prepare hybrid perovskites by changing the composition of inorganic and organic materials, to realize their spectral regulation, promoting better use in solar materials, photoelectric sensors, micro-lasers, and other optoelectronic devices.

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