Formamidinium Lead Bromide (FAPbBr$_3$) Perovskite Microcrystals for Sensitive and Fast Photodetectors

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Highlights

- Formamidinium lead trihalide (FAPbBr$_3$) microcrystal-based photodetectors facilitate efficient charge transfer.
- The fabricated FAPbBr$_3$ photodetector shows good responsivity, external quantum efficiency, and detectivity.
- Two-photon performance of the photodetectors is better than that previously reported for MAPbBr$_3$ photodetectors.

Abstract Because of the good thermal stability and superior carrier transport characteristics of formamidinium lead trihalide perovskite H$_2$NC(NH$_2$)$_2$PbX$_3$ (FAPbX$_3$), it has been considered to be a better optoelectronic material than conventional CH$_3$NH$_3$PbX$_3$ (MAPbX$_3$). Herein, we fabricated a FAPbBr$_3$ microcrystal-based photodetector that exhibited a good responsivity of 4000 A W$^{-1}$ and external quantum efficiency up to 10$^6$% under one-photon excitation, corresponding to the detectivity greater than 10$^{14}$ Jones. The responsivity is two orders of magnitude higher than that of previously reported formamidinium perovskite photodetectors. Furthermore, the FAPbBr$_3$ photodetector’s responsivity to two-photon absorption with an 800-nm excitation source can reach 0.07 A W$^{-1}$, which is four orders of magnitude higher than that of its MAPbBr$_3$ counterparts. The response time of this photodetector is less than 1 ms. This study provides solid evidence that FAPbBr$_3$ can be an excellent candidate for highly sensitive and fast photodetectors.

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1 Introduction

In recent years, photoelectric devices have been widely investigated [1–3], especially detectors with different morphologies and sizes, for exploring their mechanisms, simplifying their syntheses, and improving device efficiencies [4–10]. Photodetectors based on hybrid organo-lead trihalide perovskite CH₃NH₃PbX₃ (MAPbX₃, X = Cl, Br, I) have attracted significant attention in the optoelectronic field owing to their strong absorption coefficients (up to 10⁵ cm⁻¹) [11–14], carrier mobilities (2.5–1000 cm² V⁻¹ s⁻¹) [15–19], long carrier lifetimes (0.08–4.5 μs) [17, 19–21], and diffusion lengths (2–175 μm) [19, 20, 22, 23]. In particular, Saidaminov et al. produced a planar-integrated photodetector using MAPbBr₃ single crystals, achieving high-performance light detection in the wide wavelength range [24]. Bao et al. reported low-noise and large-linear-dynamic-range photodetectors based on MAPbBr₃ and MAPbI₃ [25]. Yang et al. demonstrated the great potential of metal–semiconductor–metal structures for low-cost and high-performance optoelectronic devices [26]. Moreover, Hu et al. [27] reported high-performance and low-working-voltage photodetectors. Further, a UV-selective photodetector based on MAPbI₃ was also demonstrated [28, 29]. However, conventional MAPbX₃ materials have poor stability [30, 31], which severely impedes device development.

2 Experimental

2.1 Chemicals and Reagents

Formamidine acetate, lead bromide (PbBr₂, > 98%) and hydrobromic acid (48 wt% in water) were purchased from Alfa Aesar. Gamma-butyrolactone (GBL) and N,N-dimethylformamide (DMF) were purchased from Kermel. All compounds were used without any further purification.

2.2 Synthesis of CH(NH₂)₂Br (FABr)

FABr was synthesized by slowly dropping 10 mL hydrobromic acid into 50 mmol (5.205 g) formamidine acetate in a flask, accompanied by continuous stirring at 0 °C for 2 h under argon atmosphere. The product FABr was formed once the solvent was removed using a rotary evaporator at 70 °C. The crude white powder was dissolved in ethanol and subsequently reprecipitated into diethyl ether. Then, the filtered product was dried at 60 °C in a vacuum oven for 24 h for further use.

2.3 Synthesis of FAPbBr₃ MCs

FAPbBr₃ MCs were grown by a modified inverse crystallization method using toluene as the antisolvent. In brief, 5 mmol PbBr₂ (1.835 g) and 5 mmol FABr (0.625 g) were dissolved in 10 mL mixed DMF:GBL (1:1 v/v) solvent at 25 °C. The solution was filtered using nylon filters with a 0.22-m pore size. Then, 1 mL precursor was diluted in 2 mL DMF and antisolvent toluene was added to obtain a saturated solution. Single crystals of FAPbBr₃ with millimeter dimensions were formed after stirring on a hot plate of 80 °C.

2.4 Device Preparation

Standard photolithography and hydrochloric acid etching were used to obtain conductive glass substrates with a channel length and width of 5 μm and 1 mm, respectively. After synthesizing FAPbBr₃ MCs using the above-described method, the substrates were deposited on these crystals and dried at 160 °C for 10 min.

2.5 Measurements and Characterizations

Scanning electron microscopy (SEM) was performed using a field-emission scanning electron microscope (JEOL, JSM-7800F, 3 kV). X-ray diffraction (XRD) was performed using an X-pert PRO diffractometer equipped with Cu K_α X-ray (λ = 1.54186 Å) tubes. UV–Vis diffuse reflectance spectra were recorded at room temperature on a
JASCO V-550 UV–Vis absorption spectrometer with an integrating sphere operating in 200–900 nm. Photoluminescence (PL) was recorded using a Horiba PTI QuantuMaster 400 system with an excitation of 470 nm. Time-resolved PL decay was obtained on the basis of the time-correlated single-photon counter (TCSPC) technology using a light-emitting diode (LED) to provide a 376-nm excitation beam. The decay data were analyzed using commercial software provided by Horiba. For trap-state density evaluation, one layer of conductive glass (ITO) undertaken the crystal film was used as one electrode. An 800-nm-thick gold (Au) layer deposited on top of the film by thermal evaporation was used as the other electrode. This structure had a rather simple geometry with the sample deposited on ITO and evaporated Au on opposite sides, and the structure should be kept in the dark. Current–voltage measurements were conducted using a Keithley 2400 source meter. For light characterization under one-photon excitation, a monochromatic source (LED, \( \lambda = 495 \) nm) was used. Spectral responsivity (\( R \)) was calculated by the photocurrent (\( I_{ph} \)) and incident power (\( P_{inc} \)) according to the relation \( R = \frac{I_{ph}}{P_{inc}} \). For two-photon irradiation, the photocurrent was generated using a femtosecond laser system (Spitfire Pro, SpectraPhysic) with an output wavelength of 800 nm and a repetition rate of 1000 Hz as the light source.

3 Results and Discussion

We synthesized FAPbBr\(_3\) MCs using a modified antisolvent-assisted inverse temperature crystallization method [8, 24, 28]. To facilitate the removal of the solvent and form homogeneous crystalline films, 1 M precursor (equimolar FABr and PbBr\(_2\) dissolved in a mixed solvent as shown in experimental section) was diluted three times in DMF. The antisolvent toluene was then added to obtain a saturated solution. This saturated solution was stirred at 80 °C to accelerate the nucleation and increase the yield of the interconnected crystals. The mean size of the as-obtained FAPbBr\(_3\) MCs was \( \sim 10 \pm 5 \) μm, as shown in the top-view SEM image (Fig. 1a). These MCs were interconnected as a continuous film with a thickness of \( \sim 150 \) μm, as shown in Fig. 1b. XRD results shown in Fig. 1c confirmed the cubic phase of the FAPbBr\(_3\) MCs [35, 39]. The MCs exhibited an absorption band edge at 570 nm, corresponding to a bandgap of 2.18 eV, as obtained from the Tauc plot of the absorption spectrum (Fig. 1d). The emission peak of the MCs appeared at 567 nm (insets of Fig. 1d), which was consistent with previous results [33, 37, 40]. Additionally, PL decay was measured using the TCSPC technology (Fig. 1e), and a fast component (\( \tau_1 = 15 \pm 1 \) ns) and slow decay (\( \tau_2 = 282 \pm 5 \) ns) reflected the surface and bulk carrier lifetimes.

![Image](image_url)
of the FAPbBr$_3$ MCs, respectively. We also conducted dark current measurements to estimate the trap-state density of the FAPbBr$_3$ MC film, as depicted in Fig. 1f. Here, the trap-state density was calculated to be $6.98 \times 10^{11}$ cm$^{-3}$ according to Eq. 1:

$$n_{\text{trap}} = \frac{2\varepsilon_0 e V_{\text{TFL}}}{qL^2}$$

where $V_{\text{TFL}}$ is the voltage at which trap states are fully filled by injected carriers, $q$ and $L$ represent the elemental charge and film thickness, respectively, $\varepsilon_0$ and $\varepsilon$ denote the vacuum permittivity and dielectric constant of FAPbBr$_3$, with $\varepsilon = 43.6$ [37]. The relatively fewer defects contributed to the formation of a high-quality film, thus promoting their application in photoelectronic devices [37, 41].

In the next step, FAPbBr$_3$ MCs were directly deposited on interdigitated ITO substrates to form the prototype photodetector device. The length and width of the gaps between neighboring digits were 5 µm and 1 mm, respectively, as shown in Fig. S1. FAPbBr$_3$ MCs covered the entire active area, forming Schottky barriers due to contact with the ITO electrode. Once a voltage was applied to the detector device, ion migration and carrier trapping occurred in the active layer and at the electrode/perovskite interfaces, respectively. This indicated that an Ohmic contact between the FAPbBr$_3$ MCs and the ITO electrode was formed. The cathode collected abundant photogenerated holes, while holes from the anode were injected into the active layer, showing the photoconductivity of the device [42–44]. The compact morphology of the MCs minimized the grain boundary and consequently diminished interfacial charge recombination. As shown in Fig. 2a, the photocurrent drastically increased with increasing excitation light intensity. In addition, the small dark current of the device (seen in Fig. S2) indicated the low carrier concentration of FAPbBr$_3$ MCs [37]. The photoresponse was also reproducible under a periodic excitation of the light pulse, as demonstrated in Fig. S3.

As shown in Fig. 2b, the photocurrent increased linearly with the incident power and the corresponding responsivity ($R$, defined as photocurrent/the incident light power) linearly decreased. The responsivity was 4000 A W$^{-1}$ at 5 V ($\lambda = 495$ nm, probe intensity = 10 nW cm$^{-2}$), which was two orders of magnitude higher than that of other FA-based perovskite photodetectors [7, 38, 45, 46]. Furthermore, the external quantum efficiency (EQE) calculated by Eq. 2 was as high as 1.05 $\times$ 10$^6$% (Fig. 2c):

$$\text{EQE} = \frac{R \cdot hc}{q\lambda}$$

In addition, the detectivity $D^*$ of the device was 3.87 $\times$ 10$^{14}$ Jones, as obtained from Eq. 3:

$$\text{Detectivity} = D^* = \frac{V_{\text{TFL}}}{R}$$
\[ D^* = \frac{R\sqrt{A}}{q I_{\text{dark}}} \]  

This value of \( D^* \) was higher than that of state-of-art MAPbI\(_3\) photodetectors (~ 10\(^{13}\) Jones) [46]. Moreover, the FAPbBr\(_3\) MC photodetector exhibited a rapid response with a rise time \( (\tau_{\text{rise}}) \) of 0.67 ms and fall time \( (\tau_{\text{fall}}) \) of 0.75 ms (Figs. 2d and S4), where \( \tau_{\text{rise}} \) and \( \tau_{\text{fall}} \) are defined as the time required for light response from 10 to 90% in the rising stage and from 90 to 10% in the falling stage, respectively.

Previous research has revealed that the photoresponse to the excitation wavelength is different for front-side excitation and back-side excitation [46]. In back-side excitation, charge carriers are efficiently collected in the vicinity of the electrodes. However, in front-side excitation, it is more difficult for charge carriers generated by short-wavelength photons to penetrate the thick film to electrodes than that of long-wavelength photons with energy comparable to the bandgap [46]. In our case, the wavelength-dependent light response using front-side excitation resembled that using back-side excitation, indicating that our device was a broadband photodetector (Figs. 3a and S5). It was found that the thickness of the FAPbBr\(_3\) microcrystalline film of about 150 \( \mu \)m allowed most photons to be transmitted through the film to generate corresponding photocurrents. Once the film became sufficiently thick (> 200 \( \mu \)m), it blocked the short-wavelength photons to the microcrystalline film to form a narrowband photodetector, which was also confirmed by Saidaminov and coworkers [46]. In addition, the generally lower photocurrent for front-side excitation could be attributed to the insufficient diffusion length of the photogenerated charges for the given film thickness, which hindered charge transportation to the bottom electrode [46]. Figure 3b shows the photocurrent variation for different bias voltages. As shown in Fig. 3c, d, when the bias voltage was decreased, the photocurrents of the photons excited far above the absorption band edge degraded more.

Perovskites have also attracted considerable attention as nonlinear semiconductor absorbers for optical limiting [47], ultrafast optical signal characterization [48], microscopy [49], and lithography [50]. Therefore, we characterized our device under two-photon excitation, where the photocurrent was generated by an 800-nm pulse laser with a photon energy much smaller than the bandgap of FAPbBr\(_3\) (2.18 eV). Figure 4a shows the PL mechanism of FAPbBr\(_3\) at 567 nm obtained under 800-nm two-photon absorption. Under 800-nm back-side illumination at a fixed bias of 5 V, the tendency of light current variation with

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**Fig. 3**  
(a) Spectral-dependent photocurrent under front-side and back-side excitation at 1 mW cm\(^{-2}\) and a bias voltage of 5 V.  
(b) Photocurrent response measured using a series of bias voltages: 2, 3, 4, and 5 V, at an excitation of 495 nm. Normalized spectral-dependent photocurrent under different bias voltages under (c) back-side and (d) front-side excitation.
respect to voltage (30–110 mW cm$^{-2}$) is provided in Fig. 4b. Under ideal conditions, the photocurrent generated by two-photon absorption showed a square ($n=2$) dependence on the input intensity [51]. However, our tested photocurrents (with $1 < n < 2$) exhibited highly dependent on incident power, which was mainly attributed to the effect of trap-state’s sub-gap absorption [8, 52]. This tendency was consistent with that reported for near-infrared CsPbBr$_3$ and MAPbBr$_3$ photodetectors [8, 51]. Consequently, the responsivity of the two-photon pumped FAPbBr$_3$ MC detector increased with increasing input intensity in the linear excitation region (Fig. 4c). The largest responsivity under 800-nm excitation (0.07 A W$^{-1}$) was much higher than that previously reported for MAPbBr$_3$ single crystals [51]. The fast response of our detector under two-photon excitation with a fast fall time (0.72 ms) is also shown in Fig. 4d. The result is similar to that observed under one-photon excitation (0.75 ms). The rapid pulse light with periodic changes was responsible for the missing rising stage.

Moreover, the amplified spontaneous emission (ASE) behavior of the FAPbBr$_3$ microcrystalline film was measured using 800-nm laser pulses with tunable intensities. The emission spectra (Fig. S6) with increasing light intensity exhibited an ASE threshold of 1.75 mJ cm$^{-2}$, which was similar to the reported two-photon ASE threshold of MAPbBr$_3$ photodetectors (2.2 mJ cm$^{-2}$) [53].

4 Conclusion

In summary, organolead trihalide perovskite FAPbBr$_3$ MCs were synthesized and then deposited as a photodetector. The photodetector exhibited a good responsivity of up to 4000 A W$^{-1}$ under back-side one-photon excitation with an EQE and detectivity of up to $1.05 \times 10^6$% and $3.87 \times 10^{14}$ Jones, respectively. Besides, the two-photon responsivity under 800-nm excitation was 0.07 A W$^{-1}$, which was four orders of magnitude higher than that reported for MAPbBr$_3$ single crystals ($10^{-6}$ A W$^{-1}$). This deposited FAPbBr$_3$ microcrystalline photodetector showed great potential for developing fast and sensitive photodetectors.

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References

1. W. Zhao, X. Xiong, Y. Han, L. Wen, Z. Zou et al., Fe-doped p-ZnO nanostructures/n-gan heterojunction for “blue-free” orange light-emitting diodes. Adv. Opt. Mater. 5(17), 1700146 (2017). https://doi.org/10.1002/adom.201700146

2. J. Zhang, X. Yang, H. Deng, K. Qiao, U. Farooq et al., Low-made.

3. W.S. Yang, J.H. Noh, N.J. Jeon, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok, High-performance photovoltaic perovskite layers fabricated through intermolecular exchange. Science 348, 1234–1237 (2015). https://doi.org/10.1126/science.aah9272

4. W. Zhang, M. Saliba, D.T. Moore, S.K. Pathak, M.T. Hörantner et al., Ultrasmooth organic-inorganic perovskite thin-film formation and crystallization for efficient planar heterojunction solar cells. Nat. Commun. 6, 6142 (2015). https://doi.org/10.1038/ncomms7142

C. Wehrenfennig, G.E. Eperon, M.B. Johnston, H.J. Snaith, L.M. Herz, High charge carrier mobilities and lifetimes in organolead tribalide perovskites. Adv. Mater. 26(10), 1584–1589 (2014). https://doi.org/10.1002/adma.201305172

D.A. Valverde-Chávez, C.S. Ponseca, C.C. Stoumpos, A. Yartsev, M.G. Kanatzidis, V. Sundström, D.G. Cooke, Intrinsic femtosecond charge generation dynamics in single crystal CH3NH3Pbl3. Energy Environ. Sci. 8(12), 3700–3707 (2015). https://doi.org/10.1039/C5EE02530F

D.N. Dirin, I. Cherniukh, Y. Shynkarenko, M.V. Kovalenko, Solution-grown CsPbBr3 perovskite single crystals for photon detection. Chem. Mater. 28(8), 8470–8474 (2016). https://doi.org/10.1021/acs.chemmater.6b04298

D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu et al., Low-trap-state density and long carrier diffusion in organolead tribalide perovskite single crystals. Science 347(6221), 519–522 (2015). https://doi.org/10.1126/science.aac2725

M.I. Saidaminov, A.L. Abdelhady, B. Murali, E. Alarousu, V.M. Burlakov et al., High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization. Nat. Comm. 6, 7586 (2015). https://doi.org/10.1038/ncomms8586

Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, Electron-hole diffusion lengths > 175 μm in solution-grown CH3NH3Pbl3 single crystals. Science 347(6225), 967–970 (2015). https://doi.org/10.1126/science.aad5760

S.D. Stranks, G.E. Eperon, G. Grancini, C. Menelau, M.J. Alvarado, T. Leijtens, L.M. Herz, A. Petrozza, H.J. Snaith, Electron-hole diffusion lengths exceeding 1 micrometer in organometal trihalide perovskite absorber. Science 342(6156), 341–344 (2013). https://doi.org/10.1126/science.1243982

M.I. Saidaminov, V. Adinolfi, R. Comin, A.L. Abdelhady, W. Peng et al., Planar-integrated single-crystalline perovskite photodetectors. Nat. Commun. 6, 8724 (2015). https://doi.org/10.1038/ncomms9724

C. Bao, Z. Chen, Y. Fang, H. Wei, Y. Deng, X. Xiao, L. Li, J. Huang, Low-noise and large-linear-dynamic-range photodetectors based on hybrid-perovskite thin-single-crystals. Adv. Mater. 29(39), 1703209 (2017). https://doi.org/10.1002/adma.201703209

J. Yang, T. Hu, K. Zhu, Q. Xu, High-gain and fast-response metal- semiconductor-metal structured organolead halide perovskite photodetectors. J. Phys. D Appl. Phys. 50(49), 495102 (2017). https://doi.org/10.1088/1361-6463/aa918c

W. Hu, R. Wu, S. Yang, P. Fan, J. Yang, A. Pan, Solvent-induced crystallization for hybrid perovskite thin-film photodetector with high-performance and low working voltage. J. Phys. D Appl. Phys. 50(37), 375101 (2017). https://doi.org/10.1088/1361-6463/aa8059

V. Adinolfi, O. Ouellette, M.I. Saidaminov, G. Walters, A.L. Abdelhady, O.M. Bakr, E.H. Sargent, Fast and sensitive solution-
processed visible-blind perovskite uv photodetectors. Adv. Mater. 28(33), 7264–7268 (2016). https://doi.org/10.1002/adma.201601196
29. G. Maculan, A.D. Sheikh, A.L. Abdelhady, M.I. Saidaminov, M.A. Haque et al., CH3NH3PbCl3 single crystals: inverse temperature crystallization and visible-blind uv-photodetector. J. Phys. Chem. Lett. 6(19), 3781–3786 (2015). https://doi.org/10.1021/acs.jpclet.5b01666
30. T.B. Song, Q. Chen, H. Zhou, C. Jiang, H.H. Wang, Y.M. Yang, Y. Liu, J. You, Y. Yang, Perovskite solar cells: film formation and properties. J. Mater. Chem. A 3(17), 9032–9050 (2015). https://doi.org/10.1039/C5TA05246C
31. X. Li, M.I. Dar, C. Yi, J. Luo, M. Tschumi, S.M. Zakeeruddin, T.B. Song, Q. Chen, H. Zhou, C. Jiang, H.H. Wang, Y.M. Yang, T.M. Koh, K. Fu, Y. Fang, S. Chen, T. Sum, N. Mathews, S.G. G.E. Eperon, S.D. Stranks, C. Menelaou, M.B. Johnston, L.M. T.J. Jacobsson, J.P. Correa-Baena, M. Pazoki, M. Saliba, K. F.C. Hanusch, E. Wiesenmayer, E. Mankel, A. Binek, P. Mhaisalkar, P.P. Boix, T. Baikie, Formamidinium-containing metal-halide: an alternative material for near-IR absorption perovskite solar cells. J. Phys. Chem. C 118(30), 16458–16462 (2013). https://doi.org/10.1021/jp411112k
32. G.E. Eperon, S.D. Stranks, C. Menelaou, M.B. Johnston, L.M. Herz, H.J. Snaith, Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells. Energy Environ. Sci. 7(3), 982–988 (2014). https://doi.org/10.1039/C3EE43822H
33. T.J. Jacobsson, J.P. Correa-Baena, M. Paozki, M. Saliba, K. Schenk, M. Grätzel, A. Hagfeldt, Exploration of the compositional space for mixed lead halogen perovskites for high efficiency solar cells. Energy Environ. Sci. 9(5), 1706–1724 (2016). https://doi.org/10.1039/C6EE00030D
34. F.C. Hanusch, E. Wiesenmayer, E. Mankel, A. Binek, P. Angloher et al., Efficient planar heterojunction perovskite solar cells based on formamidinium lead bromide. J. Phys. Chem. Lett. 5(16), 2791–2795 (2014). https://doi.org/10.1021/jz501237m
35. N. Pellet, P. Gao, G. Gregori, T.Y. Yang, M.K. Nazeeruddin, J. Maier, M. Grätzel, Mixed-organic-cation perovskite photovoltaics for enhanced solar-light harvesting. Angew. Chem. Int. Edit. 53(12), 3151–3157 (2014). https://doi.org/10.1002/anie.201309361
36. A.A. Zhumekeenov, M.I. Saidaminov, M.A. Haque, E. Alarousu, S.P. Sarmah et al., Formamidinium lead halide perovskite crystals with unprecedented long carrier dynamics and diffusion length. ACS Energy Lett. 1(1), 32–37 (2016). https://doi.org/10.1021/acsenergylett.6b00002
37. D. Yu, F. Cao, Y. Shen, X. Liu, Y. Zhu, H. Zeng, Dimensionality and interface engineering of 2d homologous perovskites for boosted charge-carrier transport and photodetection performances. J. Phys. Chem. Lett. 8(12), 2565–2572 (2017). https://doi.org/10.1021/acs.jpclett.7b00993
38. M.I. Saidaminov, A.L. Abdelhady, G. Maculan, O.M. Bakr, Retrograde solubility of formamidinium and methylammonium lead halide perovskites enabling rapid single crystal growth. Chem. Commun. 51(100), 17658–17661 (2015). https://doi.org/10.1039/C5CC06916E
39. N. Arora, M.I. Dar, M. Hezam, W. Tress, G. Jacopin et al., Photovoltaic and amplified spontaneous emission studies of high-quality formamidinium lead bromide perovskite films. Adv. Funct. Mater. 26(17), 2846–2854 (2016). https://doi.org/10.1002/adfm.201504977
40. Q. Han, S.H. Bae, P. Sun, Y.T. Hsieh, Y.M. Yang et al., Single crystal formamidinium lead iodide (FAPbI3): insight into the structural, optical, and electrical properties. Adv. Mater. 28(11), 2253–2258 (2016). https://doi.org/10.1002/adma.201505002
41. R. Dong, Y. Fang, J. Chae, J. Dai, Z. Xiao et al., High-gain and low-driving-voltage photodetectors based on organolead triiodide perovskites. Adv. Mater. 27(11), 1912–1918 (2015). https://doi.org/10.1002/adma.201405116
42. W. Hu, W. Huang, S. Yang, X. Wang, Z. Jiang et al., High-performance flexible photodetectors based on high-quality perovskite thin films by a vapor-solution method. Adv. Mater. 29(43), 1703256 (2017). https://doi.org/10.1002/adma.201703256
43. M. Ahmadi, T. Wu, B. Hu, A review on organic-inorganic halide perovskite photodetectors: device engineering and fundamental physics. Adv. Mater. 29(41), 1605242 (2017). https://doi.org/10.1002/adma.201605242
44. Y. Liu, J. Sun, Z. Yang, D. Yang, X. Ren, H. Xu, Z. Yang, S.F. Liu, 20-nm large single-crystalline formamidinium-perovskite wafer for mass production of integrated photodetectors. Adv. Opt. Mater. 4(11), 1829–1837 (2016). https://doi.org/10.1002/adom.201600327
45. M.I. Saidaminov, M. Haque, M. Savoie, A.L. Abdelhady, N. Cho et al., Perovskite photodetectors operating in both narrowband and broadband regimes. Adv. Mater. 28(37), 8144–8149 (2016). https://doi.org/10.1002/adma.201601235
46. V. Liberman, M. Rothschild, O. Bakr, F. Stellacli, Optical limiting with complex plasmonic nanoparticles. J. Opt. 12(6), 065001 (2010). https://doi.org/10.1088/2040-8978/12/6/065001
47. E. Chong, T. Watson, F. Festy, Autocorrelation measurement of femtosecond laser pulses based on two-photon absorption in gap photodiode. Appl. Phys. Lett. 105(6), 062111 (2014). https://doi.org/10.1063/1.4893423
48. W.R. Zipfel, R.M. Williams, Nonlinear magic: multiphoton microscopy in the biosciences. Nat. Biotechnol. 21(11), 1369–1377 (2003). https://doi.org/10.1038/nbt889
49. W. Haske, V.W. Chen, J.M. Hales, W. Dong, S. Barlow, S.R. Marder, J.W. Perry, 65 nm feature sizes using visible wavelength 3-D multiphoton lithography. Opt. Express 15(6), 3426–3436 (2007). https://doi.org/10.1364/OE.15.003426
50. G. Walters, B.R. Sutherland, S. Hoogland, D. Shi, R. Comin, D.P. Sellan, O.M. Bakr, E.H. Sargent, Two-photon absorption in organometallic bromide perovskites. ACS Nano 9(9), 9340–9346 (2015). https://doi.org/10.1021/acs.nano.5b03308
51. Q. Lin, A. Armin, P.L. Burn, P. Meredith, Near infrared photodetectors based on sub-gap absorption in organohalide perovskite single crystals. Laser Photonics Rev. 10(6), 1047–1053 (2016). https://doi.org/10.1002/lpor.201600215
52. B. Yang, X. Mao, S. Yang, Y. Li, Y. Wang, M. Wang, W. Deng, K. Han, Low threshold two-photon-pumped amplified spontaneous emission in CH3NH3PbBr3 microdisks. ACS Appl. Mater. Interfaces 8(30), 19587–19592 (2016). https://doi.org/10.1021/acsami.6b04246