

# Deciphering the Ultrafast Nonlinear Optical Properties and Dynamics of Pristine and Ni-Doped CsPbBr<sub>3</sub> Colloidal Two-**Dimensional Nanocrystals**

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## Supporting Information

ABSTRACT: While the unabated race persists in achieving record efficiencies in solar cells and other photonic/optoelectronic devices using lead halide perovskite absorbers, a comprehensive picture of the correlated third-order nonlinear optical (NLO) properties is yet to be established. The present study is aimed at deciphering the role of dopants in multiphoton absorption properties of intentionally engineered CsPbBr<sub>3</sub> colloidal nanocrystals (NCs). The charge separation of the plasmonsemiconductor conduction band owing to the hot electron transfer at the interface was demystified using the dynamics of the bleached spectral data from femtosecond (fs) transient absorption spectroscopy with broadband capabilities. The NLO properties studied through the fs Z-scan technique revealed that Ni-doped CsPbBr<sub>3</sub> NCs exhibited strong third-order NLO



susceptibility of  $\sim 10^{-10}$  esu. The exotic photophysical phenomena in these pristine and Ni-doped CsPbBr<sub>3</sub> colloidal twodimensional (2D) NCs reported herein are believed to provide the avenues to address the critical variables involved in the structural differences and their correlated optoelectronic properties.

Perovskite colloidal semiconductor nanocrystals (NCs)/ nanoplates (NPs) are an emerging class of nonlinear optical (NLO)/photonic materials because of their remarkable optoelectronic properties and promising applications in the field of light-emitting diodes (LEDs). The evolution of the organic-inorganic lead halide perovskites (OIHPs) has sparked research interest in both academia and industry because of OIHPs' intriguing properties. Halide perovskites possess galvanizing properties such as high carrier mobility and tunable photoluminescence (PL) and have been widely investigated in the field of photovoltaics,<sup>1,2</sup> light-emitting diodes,<sup>3-5</sup> and lasing<sup>6,7</sup> applications. To date, most of the research has been devoted to enhancing the efficient phononassisted photoluminescence (PL) up conversion and near-unity external quantum efficiencies (EQEs) of the all-inorganic perovskite quantum dots (QDs).<sup>8,9</sup> However, the profound understanding of the photophysical properties of all-inorganic lead halide perovskites (IHPs) has not been fully explored. Among the all IHP NCs,  $CsPbX_3$  (X = Cl, Br, I) based NCs are alluring candidates for promising light emitters, by virtue of their tunable (size- and composition-dependent) band gap from the violet to the near-infrared region, and also possess extremely narrow full width at half-maximum (fwhm). The added advantage is the facile tunability of their absorption

edges and emission colors via anion and or cation exchange reactions.<sup>10,11</sup>

The IHP two-dimensional (2D) colloidal NCs have been demonstrated to exhibit strong multiphoton absorption (MPA).<sup>12</sup> The semiconductor NC geometries are known to induce a promising effect on the NLO properties.<sup>13</sup> Semiconductor 2D NPs possess striking optical properties, such as narrow PL emission at room temperature together with their substantial oscillator strength, which can be altered by their vertical thickness. It is anticipated that the strong confinement in the vertical direction for perovskite 2D NCs can improve their linear optical as well as the NLO properties. These properties are the prerequisites for high performance in NLO and photonic applications. Additionally, CsPbX<sub>3</sub> NCs possess high photoluminescence quantum yields (PLQY), in some cases as high as up to 90%; narrow emission bandwidth; tunable PL emission spectra; and higher stability compared with CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, making them alluring semiconductors for next-generation optoelectronic applications.

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**Figure 1.** (a) UV-visible absorption spectra of pristine and  $Ni_{0.08}$ -doped CsPbBr<sub>3</sub>. (b) Photoluminescence spectra of pristine and  $Ni_{0.08}$ -doped CsPbBr<sub>3</sub>. The inset showing the as-synthesized NCs before (left) and after  $Ni_{0.08}$ -doped (right). (c) Time-resolved PL of all samples. All samples refer to pristine CsPbBr<sub>3</sub> and four Ni-doped CsPbBr<sub>3</sub> NCs as marked in the panel. (d) SEM image of  $Ni_{0.08}$ -doped CsPbBr<sub>3</sub> film with inset showing the EDS spectrum. (e and f) TEM images of pristine and  $Ni_{0.08}$ -doped CsPbBr<sub>3</sub> with insets illustrating the HRTEM images and the SAED patterns. "a.u." stands for arbitrary units.

The structure-property correlation of CsPbX<sub>3</sub> perovskite NCs can be achieved by means of particle size modulation or introducing different halide ions. Importantly the shape of colloidal NCs alters the physiochemical properties and also the optoelectronic properties for effective utilization in diverse applications. Very limited reports are available on shape control synthesis of CsPbBr<sub>3</sub> NCs with bright blue emission. Impurity doping is one of the plausible ways of introducing novel functionalities into traditional semiconductors to induce p- and n-type behaviors.<sup>14</sup> Heterovalent ion doping such as Bi<sup>3+</sup> and rare earth ions or isovalent ions such as Mn<sup>2+</sup> into lead halide perovskites results in the occurrence of new emission bands attributed to dopant-related emitters.<sup>14-21</sup> Yong et al. reported that the Ni<sup>2+</sup> doping enhanced short-range order of perovskite NCs for near-unity PLQY.<sup>22</sup> Additionally, Ni<sup>2+</sup> ions, as dopant, exhibit a strong inclination for octahedral coordination with halide ions.<sup>23</sup> Herein, we report the synthesis of pristine and Ni-doped colloidal CsPbBr<sub>3</sub> 2D NCs through the reprecipitation method. The effect of nickel doping on NLO properties of CsPbBr<sub>3</sub> colloidal 2D NCs is understood using the Z-scan technique. The optimized nickel doping in CsPbBr<sub>3</sub> is found to increase the third-order NLO susceptibility to  $\sim 10^{-10}$  esu. We believe that the analyses reported in the current work can address the critical variables involved in the dopant-induced structure-property correlations in CsPbBr<sub>3</sub> NCs. Furthermore, detailed femtosecond (fs) transient absorption studies are performed to understand the role of doping on the excited-state dynamics, providing information on the utility of these materials in solar cell applications.

In a typical synthesis of colloidal 2D NCs, reported elsewhere,<sup>24</sup> we have intentionally engineered CsPbBr<sub>3</sub> perovskite to yield the flat 2D NCs by reacting Cs-oleate with PbBr<sub>2</sub> in dry octadecene (ODE) solution with long-chain capping ligands via oleic acid and oleyl amine in appropriate proportions. The detailed synthesis is found in the Experimental Section in the Supporting Information. Because strong confinement in the vertical direction of 2D NCs is anticipated, we aimed at synthesizing the NCs mentioned above to study the linear and NLO properties. For ease of representation, we consider the doping percentages of Ni as  $Ni_x$  (*x* varied from 0.03 mM to 0.1 mM) throughout the text. The desirable and optimized steady-state optical properties are observed in  $Ni_{0.08}$ ; hence, we have considered the  $Ni_{0.08}$  doping as the representative dopant level in the following sections.

Figure 1a,b illustrates the absorption/PL spectra originating from pure and Ni<sub>0.08</sub>-doped CsPbBr<sub>3</sub> colloidal 2D NCs. The absorption peaks of CsPbBr3 and Ni008-doped CsPbBr3 are near 482 and 508 nm, while the emission peaks are located at 530 and 566 nm. No new absorption bands are introduced by Ni doping, and the excitation absorption of NCs shifts to the red. A significant red shift of the absorption edge and improved visible light absorption are observed for the Ni<sub>0.08</sub>-doped samples when compared with the pristine sample. A similar trend is observed in both the absorption and emission spectra upon the increase in the dopant concentration (Figure 1a,b), which is accompanied by decreased fwhm for the doped NCs. The possible reason for the spectral shift may be the size change upon doping, which alters the absorbing and emitting states in NCs. The PL spectra fwhm values were 17.78 nm for Ni<sub>0.08</sub>-doped CsPbBr<sub>3</sub> NCs and 18.37 nm for pristine CsPbBr<sub>3</sub> NCs (Figure 1b). The decreased PL spectra fwhm for doped NCs can be attributed to the uniform size distribution of Nidoped CsPbBr<sub>3</sub> 2D colloidal NCs.

Interestingly the morphology of doped NCs remained the same at least for 30 days when exposed in the ambient environment. The Ni<sub>0.08</sub>-doped CsPbBr<sub>3</sub> showed maximum bathochromic shift when compared to pristine CsPbBr<sub>3</sub>, which



**Figure 2.** (a-e) TA spectra of all the samples excited at 400 nm wavelength for different probe delay times. (f-j) Bleach recovery dynamics of all samples near bleach maximum. Symbols are the experimental data, while the solid lines are the theoretical fits. All samples refer to pristine CsPbBr<sub>3</sub> and four Ni-doped CsPbBr<sub>3</sub> NCs as marked in the figure.

is attributed to the introduction of additional energy levels within the band gap of CsPbBr<sub>3</sub> due to Ni doping resulting in a decrease in the band gap of CsPbBr<sub>3</sub> from 2.28 to 2.24 eV. A noticeable change in the band gap energy (Figure 1a) and a clear color difference (Figure 1b inset) is observed for pristine CsPbBr3 and Ni-doped CsPbBr3, further confirming the incorporation of Ni ions at the Pb sites. The bathochromic shifted emission peak of Ni-doped CsPbBr3 compared with pure CsPbBr<sub>3</sub> may be due to the alteration of band gap energy due to the doping. The fluorescent lifetime values were calculated from time-resolved photoluminescence (TRPL) spectra to estimate the lifetime of photogenerated charge carriers (Figure 1c). The fluorescence decay is slower for Ni<sub>0.08</sub>-doped CsPbBr<sub>3</sub> NCs when compared with pristine CsPbBr<sub>3</sub> NCs. The Ni<sub>0.08</sub>-doped CsPbBr<sub>3</sub> colloidal 2D NCs were found to exhibit the highest lifetime values (13.41 ns) compared with pristine (11.38 ns) and other Ni-doped samples. The colloidal 2D NCs are highly susceptible to surface defects because of a large surface-to-volume ratio, suggesting their lifetimes are relatively low, which is an added advantage for utilization in the LED devices. Interestingly the Ni doping is anticipated to form additional defect states within the band gap because of Ni doping that can increase the lifetimes of charge carriers. These values suggest that recombination of photogenerated charge carriers in Ni<sub>0.08</sub>doped CsPbBr<sub>3</sub> is slower.

Morphological scanning electron microscopy (SEM) investigations on the Ni-doped drop-casted densely packed film clearly indicated the sample contained square-shaped NCs which were further confirmed from the transmission electron microscopy (TEM) imaging. The incorporation of the Ni doping into the CsPbBr<sub>3</sub> lattice is confirmed from the elemental EDS mapping (Figure 1d). TEM micrographs (Figure 1e,f) depict the as-synthesized pristine and  $Ni_{0.08}$ doped CsPbBr<sub>3</sub> to be square shaped 2D NCs with an average particle size of ~20 nm. Bright lattice fringes with a lattice plane distance of 0.317 nm are observed for Ni-doped CsPbBr<sub>3</sub> NCs, which matches with the orthorhombic phase of CsPbBr<sub>3</sub>. This indicates that the growth direction may be bound for flat facets. Strong and bright diffraction spot arrays in the SAED pattern indicate that the CsPbBr<sub>3</sub> NCs possess a well-defined crystalline structure (insets of Figure 1e,f). Notably, in Ni<sub>0.08</sub>doped CsPbBr<sub>3</sub>, the size distribution of NCs narrowed, which is in agreement with previously reported results indicating that the doping could influence the size and uniformity of NCs, as revealed by low-magnification and high-resolution TEM.<sup>22</sup> The EDS spectral data further confirmed that the prepared Ni<sub>0.08</sub>doped CsPbBr<sub>3</sub> NCs composed of Cs, Pb, Ni, and Br elements. The elemental mapping results of a selected area of the SEM image of Ni<sub>0.08</sub>-doped CsPBBr<sub>3</sub> sample suggest the coexistence of the constituent elements (Cs, Pb, Ni, and Br). The image (Figure S1) shows no clustering of particular components, suggesting that all elements are homogeneously distributed and in a disperse state throughout the sample. The atom ratio of the three elements was calculated to be around 1:1:3 (Figure **S**1).

The transient absorption (TA) spectra of  $CsPbBr_3$  samples are characterized (see Figure 2a) by a broad absorption in the spectral region >512 nm and an exciton bleach consisting of a peak near 500 nm (PB1) which, possibly, can be assigned to

time constant	CsPbBr <sub>3</sub>	0.03% Ni-doped	0.05% Ni-doped	0.08% Ni-doped	0.1% Ni-doped
$ au_1$ (ps)	$1.6 \pm 0.2$	$2.7 \pm 0.1$	$2.4 \pm 0.03$	$3.2 \pm 0.7$	$2.5 \pm 0.05$
$\tau_2$ (ps)	$52 \pm 1.7$	$36 \pm 2.7$	$26.4 \pm 1.2$	$30.1 \pm 1.5$	$34 \pm 2.1$
$ au_3$ (ps)	$305 \pm 9$	$195 \pm 3.8$	$250 \pm 5.8$	$200 \pm 3.2$	$277 \pm 6.5$

Table 1. Decay Time Constants of Bleach Maximum of All the Perovskite NCs Investigated in This Study



Figure 3. Z-scan open (a-e) and closed (f-j) aperture curve of all samples measured at 800 nm. Open circles are the experimental data, and the solid lines are the theoretical fits. All samples refer to pristine CsPbBr<sub>3</sub> and four Ni-doped CsPbBr<sub>3</sub> NCs as marked in the figure.

the band gap renormalization and state filling.<sup>25</sup> The exciton bleach maximum is fitted with a triple exponential function Y = $Y_0 + A_1 \exp[-(x - x_0)/\tau_1] + A_2 \exp[-(x - x_0)/\tau_2] +$  $A_3 \exp[-(x - x_0)/\tau_3]$ ; the data is shown in Figure 2f-j for all the samples, and the obtained three time constants are summarized in Table 1 (fittings are performed in Matlab and surface Xplorer). The fast component of the CsPbBr<sub>3</sub> NCs (<1.63 ps) could be attributed to the intraband relaxation time, and the longer lifetime of  $\sim$ 50 ps is probably due to the relaxation of the carriers into the trap states; the longest component ( $\tau_{3}$ , 195–305 ps) can be assigned to the exciton recombination time. The 400 nm excitation creates excitons above the band-edge, and therefore, the slowest component can be assigned to the cooling of these hot excitons to the band-edge excitonic state (intraband relaxation), which typically transpires in the picosecond time scale in such materials. For example, see an excellent review article discussing all such physical mechanisms by Mondal et al.<sup>16</sup>

The TA signal of Ni-doped CsPbBr<sub>3</sub> 2D NCs depicted a narrower plasmon bleach signal near 450 nm (Figure S3). At lower doping concentrations (0.03, 0.05, and 0.08 mM of Ni), the TA signals at plasmonic bleach decayed within 0.3 ps, and at higher concentration (0.1 mM), it stayed up to 1 ps. This

clearly shows the likelihood of coupling between the Ni and CsPbBr<sub>3</sub>.<sup>26</sup> The bleach signal of Ni-CsPbBr<sub>3</sub> NCs is observed to be sandwiched between two positive signals of photoinduced absorption (PIA) centered at 450-490 nm (PIA1) and >530 nm (PIA2) because of the hot charge carrier absorption.<sup>27</sup> A second bleach signal, depicted in Figure 2b, appearing at 500 nm (PB2) can be attributed to hot exciton induced bleach, and it recovers quickly through broadening of the PIA1. The peak positions of ground-state bleach (GSB) shows a red shift with the delay time (Figure 2), which is most likely due the state filling of the initially generated hot excitons.<sup>26</sup> It has been observed that the oscillation strength of perovskite NCs is perfect for efficient hot electron conversion near the metal/semiconductor interfaces.<sup>28,29</sup> From Figure S3 data it is also observed that the TA signals have a slow rise up to 5 ps, which may be due to the plasmon hot electron transfer between metal-semiconductor interfaces.<sup>26</sup> The TA signal of 0.1 mM Ni depicted a faster rise compared to other samples. The plasmon bleach at 450 nm of Ni-doped NCs (for example, see the data of 0.1 mM Ni presented in the Figure S4) was fitted with a double exponential function, having a fast component of 0.2 ps and a slow component of 2.5 ps. Huang et al. recently reported the plasmon-induced hot

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sample	$\alpha_2 ~({\rm cm/W})$	$\sigma^{(2)}~{ m GM}$	$n_2  ({\rm cm}^2/{\rm W})$	$\chi^{( m R)}~(m^2/V^2)$	$\chi^{(\mathrm{I})}~(\mathrm{m}^2/\mathrm{V}^2)$	$\chi^{(3)}~(\mathrm{m^2/V^2})$	$\chi^{(3)}$ (esu)
CsPbBr <sub>3</sub>	$3.9 \times 10^{-11}$	$1.6 \times 10^{4}$	$3.52 \times 10^{-12}$	$4.13 \times 10^{-18}$	$2.9 \times 10^{-22}$	$4.12 \times 10^{-18}$	$3.0 \times 10^{-10}$
0.03% Ni-doped	$3.8 \times 10^{-11}$	$1.56 \times 10^{4}$	$7.9 \times 10^{-12}$	$9.26 \times 10^{-18}$	$2.83 \times 10^{-22}$	$9.26 \times 10^{-18}$	$6.63 \times 10^{-10}$
0.05% Ni-doped	$3.9 \times 10^{-11}$	$1.6 \times 10^{4}$	$8.4 \times 10^{-12}$	$9.8 \times 10^{-18}$	$2.91 \times 10^{-22}$	$9.8 \times 10^{-18}$	$7.0 \times 10^{-10}$
0.08% Ni-doped	$9.98 \times 10^{-11}$	$4.11 \times 10^{4}$	$8.4 \times 10^{-12}$	$9.8 \times 10^{-18}$	$7.45 \times 10^{-22}$	$9.8 \times 10^{-18}$	$7.0 \times 10^{-10}$
0.1% Ni-doped	$10.0 \times 10^{-11}$	$4.12 \times 10^{4}$	$7.85 \times 10^{-12}$	$9.2 \times 10^{-18}$	$6.34 \times 10^{-22}$	$9.2 \times 10^{-18}$	$6.6 \times 10^{-10}$

Table 3. Summary of the NLO Coefficients (2PA) and the Cross Sections of Recently Reported Perovskite Nanomaterials

perovskite material	excitation details	$\beta$ (cm/GW)	$\sigma_2$ (GM)	ref
(NCs) CsPbBr <sub>3</sub>	800 nm, 1 kHz, 90 fs		$2.7 \times 10^{6}$	40
(NCs) CsPbBr <sub>3</sub>	800 nm, 1 kHz, 100 fs	0.097	$1.2 \times 10^{5}$	41
(NPs) Mn <sup>2+</sup> -CsPbCl <sub>3</sub> (NPs) CsPbCl <sub>3</sub>	620 nm,1 kHz, 100 fs		$3.6 \times 10^5 \ 0.87 \times 10^5$	42
(NPs) CsPbBr <sub>2.7</sub> I <sub>0.3</sub>	830 nm,1 kHz, 100 fs		$4.1 \times 10^{6}$	43
(NCs) Mn <sup>2+</sup> -CsPbCl <sub>3</sub>	720 nm, 1 kHz, fs pulses		$3.18 \times 10^{5}$	44
(NCs) CsPbBr <sub>3</sub>	800 nm, 1 kHz, 100 fs		$7.1 \times 10^{5}$	45
(QDs) CsPbI <sub>3</sub>	700 nm, 80 MHz, 100 fs		$2.1 \times 10^{6}$	46
$MAPbBr_3/(OA)_2PbBr_4$	1050–2000 nm, 50 fs, 1 kHz		$3.0 \pm 0.4 - 37 \pm 6 \times 10^{6}$	47
(NCs) CsPbBr <sub>3</sub> R-Pero-NC	800 nm, 1 kHz, 100 fs		$3.68 \times 10^4$	48
CsPbBr <sub>3</sub>	1000 nm, 50 Hz, 30 ps	$5.0 \pm 0.5$		32
(QDs) CsPbCl <sub>2</sub> Br CsPbClBr <sub>2</sub> CsPbBr <sub>3</sub>	800 nm, 1 kHz, 50 fs	0.054	$1.1 \times 10^{5}$	49
		0.064	$1.6 \times 10^{5}$	
		0.091	$2.2 \times 10^5$	
Fe <sup>3+</sup> -doped CsPb(Cl/Br) <sub>3</sub>	800 nm, 80 MHz, 140 fs	210		50
MAPbX <sub>3</sub> (MA = $CH_3NH_3$ and X = $Cl$ , Br, I) bulk single crystals	532 nm, 50 Hz, 30 ps	$23 \pm 2$		51
$(C_4H_9NH_3)_2(NH_2CHNH_2)Pb_2Br_7$	1030 nm, 100 Hz, 350 fs	$5.76 \times 10^{3}$		52
CH <sub>3</sub> NH <sub>3</sub> PbBr <sub>3</sub> single crystal	800 nm, 76 MHz, 100 fs	8.6		53

electron transfer process to be as fast as <100 fs in Ag-doped CsPbBr<sub>3</sub> NCs.<sup>26</sup> The dynamics of the bleached spectral data from Table 1 confirms that with doping the fastest decay time ( $\tau_1$ ) was slower compared to pure CsPbBr<sub>3</sub>. This could be due to the charge separation of the plasmon-semiconductor conduction band owing to the hot electron transfer at the interface.<sup>26</sup> Rana et al. investigated the Fe-doped CsPbCl<sub>3</sub> perovskite and they have confirmed the energy transfer from hot exciton and band edge exciton of host to Fe<sup>3+</sup> within 135 ps.<sup>8</sup> All the time constants obtained from the fits to the experimental data are summarized in Table 1.

The NLO properties of Ni-doped CsPbBr<sub>3</sub> 2D NCs were measured at a wavelength of 800 nm using 70 fs, 1 kHz repetition rate pulses using the standard Z-scan experimental technique. Complete details of the Z-scan experiments have been reported in our previous work.<sup>30</sup> The experiments were carried at a peak intensity of ~90 GW/cm<sup>2</sup> in solution phase for both the open and closed aperture regimes. Panels a–e of Figure 3 illustrate the open aperture Z-scan data, while panels f–j depict the closed-aperture Z-scan data for all the samples investigated.

A significant value of two-photon absorption (2PA) cross section is obtained for Ni-doped CsPbBr<sub>3</sub> NCs compared to pure CsPbBr<sub>3</sub>, which could be due to the strong coupling between plasmon-excitons within the NCs. The 2PA cross sections were obtained using eq 1:

$$\sigma_n = \frac{(\hbar\omega)^{n-1}}{N} \alpha_n \tag{1}$$

where *n* is the order of the absorption coefficient,  $N(C \times N_A)$  the concentration, and  $\hbar \omega$  the incident photon energy.

The NLO coefficients and cross sections obtained from this study are summarized in Table 2. Many other research

groups<sup>31-38</sup> have investigated the NLO properties of CsPbBr<sub>3</sub> NCs, wherein they report strong 2PA mainly arising from the strong quantum confinement effect and defect states.<sup>31</sup> From Table 2, it is evident that Ni-doped CsPbBr<sub>3</sub> NCs possessed higher 2PA cross section values compared to pure CsPbBr<sub>3</sub> NCs. Higher values of  $\chi^{(3)}$  were also reported for Ni-doped CsPbBr<sub>3</sub>, and this enhancement in  $\chi^{(3)}$  can be attributed to the localized surface plasmon-induced charge transfer (at the metal-semiconductor interface).<sup>26</sup> The closed aperture Z-scan measurements revealed a self-focusing effect  $(n_2 > 0)$ , at 800 nm wavelength, and the obtained curves were fitted using the standard equations (see the Supporting Information for details). The magnitude of  $n_2$  was obtained by fitting the CA data, and obtained values of  $n_2$  were  $\sim 10^{-12}$  cm<sup>2</sup>/W (see Table 2). The enhancement in the NLO parameters of perovskite NCs usually arises from either the quantum confinement of the excitons or due to the resonant excitation of NCs. The obtained NLO coefficients are compared to some of the recently reported works on perovskite NCs.<sup>31</sup> The obtained NLO coefficients of the Ni-doped CsPbBr<sub>3</sub> are slightly lower than those reported in our previous studies on CsPbBr<sub>3</sub> nanocubes and nanorods.<sup>34</sup> However, in that particular case the measurements were performed in thin films. Recently, Suarez et al. investigated the NLO properties of polycrystalline CsPbX<sub>3</sub> nanoparticles and films, and they have found the values of  $\alpha_2$  to be ~10<sup>-11</sup> cm/W and  $n_2$  to be 10<sup>-13</sup> cm<sup>2</sup>/W obtained with fs laser pulses excitation at a repetition rate of 1 kHz.<sup>39</sup> Pramanik et al.<sup>46</sup> reported a 2PA cross section value of  $2.1 \times 10^6$  GM from CsPbCl<sub>3</sub> QDs with 100 fs pulses at 80 MHz repetition rate. He et al.42 have demonstrated multiphoton absorption from colloidal Mn-doped CsPbCl<sub>3</sub> 2D nanoplatelets and reported a 2PA cross section value of 3.6  $\times$ 10<sup>5</sup> GM. Similar studies were performed by He et al.<sup>44</sup> on

CsPbCl<sub>2</sub> NCs, and they have achieved a similar value of 2PA cross section of  $3.18 \times 10^5$  GM with fs pulse excitation at 1 kHz repetition rate. Chen et al.<sup>47</sup> have recorded a higher 2PA cross section value of  $\sim 10^6$  GM from multidimensional coreshell MAPbBr<sub>3</sub>/(OA)<sub>2</sub>PbBr<sub>4</sub> NCs with diameter of 9-10 nm while exciting with 50 fs, 1 kHz pulses. Chen et al.48 have observed 2PA-based unconverted circularly polarized luminescence from CsPbBr<sub>3</sub> with a 2PA cross section value of  $3.68 \times$ 10<sup>4</sup> GM with fs pulses. The obtained value matches with our results obtained from the present study. Han et al. investigated the 2PA from CsPbX<sub>3</sub> (X = Cl, Br, I) QDs with sizes of 10-13nm size, and they have observed 2PA with magnitudes of  $\sim 10^{-11}$  cm/W with fs pulses.<sup>49</sup> It is evident that the obtained 2PA coefficients from our study are stronger. Zou et al. also studied 2PA from the Fe<sup>2+</sup>-doped CsPbBr<sub>3</sub> microwires (with 5  $\mu$ m width and mm length), and they have obtained a 2PA value of 210 cm/GW with 80 MHz, 140 fs laser pulses.<sup>5</sup> However, it is well-established that with MHz pulse excitation the thermal contribution is dominant on the nonlinearities observed, and therefore, the NLO coefficient magnitudes are definitely higher than those obtained with kHz pulses, wherein the thermal effects are insignificant. Also, the obtained refractive index  $(n_2)$  coefficients are higher in magnitude compared to a few of the recently reported perovskites.<sup>3</sup> The summary of comparison of the NLO coefficients is provided in Table 3. Clearly the coefficients observed in the present case are on par with (or superior to) some of the recently reported values of various perovskite QDs. An error of  $\pm$ 5% in the coefficients presented here arises from the errors in peak intensity estimation, input laser power fluctuations, and fitting errors.

In summary, colloidal Ni-doped CsPbBr<sub>3</sub> 2D NCs have been investigated for photophysical properties using the fs-TAS technique. The Ni-doped and pristine CsPbBr<sub>3</sub> 2D NCs spectral properties are consistent with the strong vertical quantum confinement that are characteristics of 2D NCs. The 2PA cross sections were also investigated by using the Z-scan technique. Strong 2PA coefficients are obtained for Ni-doped CsPbBr<sub>3</sub> when compared with the pristine CsPbBr<sub>3</sub>. This may be due to the strong coupling between plasmon-excitons within the NCs. Further, the Ni-doped CsPbBr<sub>3</sub> 2D NCs demonstrated an enhanced 2PA cross section of  $4.1 \times 10^4$  GM, which is greater than that of CsPbBr<sub>3</sub> 2D NCs ( $1.6 \times 10^4$ GM). This enhanced 2PA cross section value may be due to the localized surface plasmon-induced charge transfer. The third-order NLO susceptibility values of Ni-doped CsPbBr<sub>3</sub> NCs were found to be superior ( $\chi^{(3)} \approx 10^{-10}$  esu) in the solution phase. The comparison between CsPbBr3 and Nidoped CsPbBr<sub>3</sub> NCs provide us with opportunities to understand the structural difference and their correlated optical properties and can be used for various applications, such as multiphoton bioimaging and upconverted lasing.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.9b02244.

Experimental methods, including the synthesis of NCs, elemental mapping, TAS spectra, and Z-scan calculations (PDF)

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#### Notes

The authors declare no competing financial interest.

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