Solution-processed lead iodide for ultrafast all-optical switching of terahertz photonic devices

Manjappa, Manukumara; Solanki, Ankur; Kumar, Abhishek; Sum, Tze Chien; Singh, Ranjan

2019

Manjappa, M., Solanki, A., Kumar, A., Sum, T. C., & Singh, R. (2019). Solution-processed lead iodide for ultrafast all-optical switching of terahertz photonic devices. *Advanced Materials*, 31 (32), 1901455-. doi:10.1002/adma.201901455

<https://hdl.handle.net/10356/138379>

<https://doi.org/10.1002/adma.201901455>

This is the peer reviewed version of the following article: Manjappa, M., Solanki, A., Kumar, A., Sum, T. C., & Singh, R. (2019). Solution-processed lead iodide for ultrafast all-optical switching of terahertz photonic devices. *Advanced Materials*, 31 (32), 1901455-. doi:10.1002/adma.201901455, which has been published in final form at 10.1002/adma.201901455. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

Downloaded on 26 Apr 2023 23:07:30 SGT

Solution processed Lead Iodide (PbI₂) based Photonic devices for Sensitive and Ultrafast Photo-switching applications

Manukumara Manjappa^{1,2}, Ankur Solanki^{1,*}, Abhishek Kumar^{1,2,*}, Tze Chien Sum^{1,‡} and Ranjan Singh^{1,2,†}

¹*Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore*

²*Center for Disruptive Photonic Technologies, The Photonics Institute, 50 Nanyang Avenue, Nanyang Technological University, Singapore 639798*

*These authors contributed equally to this work.

Corresponding authors: [‡]tzechien@ntu.edu.sg, [†]ranjans@ntu.edu.sg.

Keywords: ultrafast tunable metasurface, Purcell enhancement, solution processed lead iodide, ultrafast dynamics, time resolved terahertz spectroscopy.

The solution processed lead iodide (PbI₂) molecules govern the charge transport and lasing characteristics in the hybrid metal halide perovskites. Besides being a precursor in enhancing the efficiency and performance of perovskite based solar cells, PbI₂ alone offers excellent optical and photo-responsive properties that have remained elusive. Here, we experimentally probe the photo-physics and the charge carrier dynamics of the solution processed PbI₂ thin film using time resolved terahertz spectroscopy. Our results reveal the high photoconductivity and picoseconds scale ultrafast relaxation of photocarriers in PbI₂ thin film that are shown to favor the realization of sensitive and ultrafast tunable metamaterials. The resonances are completely switched off and recovered within the ultrafast timescale of 150 ps for PbI₂ spin coated terahertz asymmetric split ring (TASR) metamaterial at low pump fluence of 400 $\mu\text{J cm}^{-2}$. Further, we reveal the localized plasmon and free electron interactions in the hybrid PbI₂-TASR sample that shows film thickness dependent enhancement in the photoconductivity and relaxation lifetimes of the photo-excited PbI₂ thin-film. These results provide novel and simple techniques for realizing ultrafast tunable photonic devices and could boost the plasmonic platforms for tailoring the dynamical properties in the soft semiconducting thin-film materials such as perovskites and 2D materials.

Introduction

Over years the plasmonic micro-nanocavities have created exceptional opportunities in enhancing the light-matter interactions, which has shown wide range of applications in the areas of spectroscopy, chemical-biological sensing, lasing and nonlinear optics. Particularly, metamaterial based plasmonic cavities with strong field confinement coupled to the dynamic materials has given the ability to precisely manipulate the light-matter interactions that has led to the fascinating developments in lasing spasers^[1,2], plasmonic sensors^[3,4], optical memory devices^[5] and more recently the realization of new regime of ultrastrong polaritonic coupling^[6-8]. Further, integrating the semiconducting materials on the plasmonic micro/nanocavities provides an exciting platform for probing various resonant and non-resonant interactions with the ability to modify the properties of the semiconducting material in a controlled manner. In the recent times, the plasmonic micro-nanocavities possessing large Purcell factors^[9] are being extensively used to resonantly enhance the photon emission rates^[10-12] and the nonlinear properties^[13] of the semiconducting material in a cavity light-matter interaction regime. Such resonant interactions have also revealed strong plasmon mediated resonant quasiparticles coupling^[14], polaritonic lasers^[15], molecular vibrational mode sensing^[16] of various thin-film molecules in the near- and mid-infrared frequencies. Alongside, in the far-infrared and THz frequencies there is a large growing interest in realizing the plasmonic enhancement of the nonlinear properties of semiconducting materials for intense generation of THz waves^[17,18]. However, there exist no direct investigations related to understanding the interaction of the low frequency plasmons with the free carriers of the semiconducting materials in their nonequilibrium regime. In the recent past, using the photoconductive properties of semiconducting materials to dynamically tune the metamaterial resonance have demonstrated active and tunable metamaterials at THz frequencies. Interfacing the metamaterial with the dynamic materials such as graphene,^[19] liquid crystals,^[20] semiconductors,^[21,22] 2D transition metal dichalcogenides^[23], phase change materials,^[24,25] and superconductors^[26] has shown to be a robust way to actively control the resonance features in metamaterials across infrared and terahertz frequencies. Nevertheless, in terms of enhancing their practical applications and technological relevance, currently there is a huge quest for ultrafast switchable/tunable metasurfaces that possess low input threshold and easy fabrication techniques.

Recent progress and new approaches on tunable metasurfaces based on spin-coating and thermal evaporation of semiconductors on the metamaterial structures have given promising pathways

for realizing sensitive and ultrafast devices. Among them the solution processed organic-inorganic semiconductors such as perovskites have shown promising pathways in realizing tunable metasurfaces with their easy fabrication techniques and excellent photoresponsive properties. In the most recent studies performed by our group and A. Chanana et al., have respectively shown the ultrasensitive and wavelength dependent reconfiguration of the metamaterial resonances using solution processed perovskites layers spin coated on the metamaterial structures. However, the switching speed in these devices is limited to nano-micro seconds that is dictated by the recombination lifetimes of the photoexcited free carriers in the perovskite thin films. Here, we show the ultrafast switchable metamaterial device possessing a switching time of less than 150 ps using the solution processed lead-iodide (PbI_2) thin film on the metamaterial structures. The solution processed PbI_2 molecule is well known for its photocell applications, where it plays a precursor role in dictating the performance and quality of the perovskite based photovoltaic devices. Recent studies have shown by varying the initial mole fractions of PbI_2 in methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) perovskites is shown to alter the steady state absorption and the ultrafast carrier dynamics of the perovskite material.^[44] In addition to the beneficial characteristics of PbI_2 in enhancing the efficiency and performance of the perovskite solar cells, they alone exhibit excellent optical properties as a detector material with high stability, high quantum efficiency and good charge transporting characteristics. In the past, single crystals of PbI_2 molecules have shown to be efficient, low noise and high energy resolution γ - and X-ray detectors at room temperature.^[45,46] Furthermore, the femtosecond transient absorption study on the PbI_2 colloidal nanoparticles has shown the ultrafast electronic relaxation decay constants in the PbI_2 that ranges from 6 ps to 75 ps depending on the solvent of interest that is used in the preparation process.^[47,48] Although significant amount of investigations have been performed in order to see the effect of PbI_2 in the performance of perovskite thin-films, the photo-generated charge carrier dynamics and photoconductive properties of the solution processed PbI_2 thin-film molecules alone are yet to be investigated thoroughly.

In this work, we experimentally probe the photocarrier dynamics and the pump fluence dependent photoconductivity of the solution processed lead iodide (PbI_2) thin-film using the time resolved terahertz spectroscopy. We show that the PbI_2 thin-film sample exhibits excellent photoresponsive properties and ultrafast carrier relaxation dynamics, which are further used to

demonstrate a facile and ultrafast tunable metasurface at terahertz frequencies. We observe the interactions between the localized plasmons and the photoexcited free carriers in the thin-film resulting in the modified photoconductivity and the recombination lifetimes of the PbI_2 thin-film spin coated on the metamaterial structure. Consequently, the relaxation lifetime of the photocarriers is shortened and the photoconductivity of the thin-film is enhanced, further showing strong dependence on the thickness of the spin coated PbI_2 thin-film. Therefore, spin-coating technique of PbI_2 thin-film on the metamaterials provides a reliable platform for realizing low-cost and ultrafast tunable metamaterial based photonic devices across the terahertz and infrared frequencies. Furthermore, this method would facilitate to enhance and control the properties of the semiconducting materials through plasmon-electron coupling in the THz and far-infrared frequencies, where the studies on plasmon enhanced interactions are still elusive.

PbI_2 thin film sample characterization

The lead iodide (PbI_2) thin-film was prepared using the conventional solution-based fabrication protocol (see Experimental Methods section). Figure 1(a) depicts the atomic force microscopy (AFM) image of the solution processed PbI_2 thin-film sample spin coated on the z -cut quartz substrate (1cm x 1cm). We considered three different thicknesses of the spin coated PbI_2 samples and were estimated to be around $d_{\text{PbI}_2} = 160 \text{ nm}$, 500 nm and $2.5 \text{ }\mu\text{m}$, using the surface profilometry measurements (shown in the inset of Fig. 1(b) and in the Supporting Information). Measured X-ray diffraction (XRD) data of the thin-film sample shown in Fig. 1(b) verifies the composition and the purity of the solution processed PbI_2 film.^[49] The observed diffraction peaks (001) at 12.65° , (101) at 25.5° and (003) at 38.65° are in accordance with the standard XRD data for PbI_2 available from Joint Committee on Powder Diffraction Standards (JCPDS) database reference number 07-0235. The elucidation of ultrafast charge carrier dynamics in the solution processed PbI_2 film was performed using time resolved terahertz spectroscopy (TRTS) operating in the transmission mode. TRTS measurements provide direct and noninvasive spectroscopic approach to accurately determine both real and imaginary parts of optical constants of the sample without the need for Kramers-Kronig transformations. In our measurements, the sample was pumped with an optical pulse of photon energy 3.09 eV ($\lambda = 400 \text{ nm}$), which is frequency doubled from the amplified femtosecond optical pulse of repetition rate 1 kHz and the energy 6 mJ per pulse. The photon energy of the optical pulse is higher than the energy band gap ($E_g \sim 2.2$

eV) of the PbI₂ thin-film sample. Terahertz beam is used as the probe to capture the change in the transmission through the sample under the influence of the varying fluence and delay time of the optical excitation pulse. Further technical details on the TRTS measurements are given in the Experimental Methods.

Ultrafast relaxation dynamics of the PbI₂ thin film

Optical excitation of PbI₂ thin-film sample with the pulse of energy (3.09 eV) greater than the energy band gap of the PbI₂ ($E_g = 2.2$ eV) results in the inter-band excitation of the electrons from the valance band to the conduction band. The free-carriers excitation and their recombination dynamics in 160 nm thin PbI₂ film are revealed as the change in THz transmission ($-|\Delta E/E|$) and the time dependent photoconductivity ($\Delta\sigma(t_p)$) plots, as shown in Fig. 1(c) and (d). Analysis of the observed ultrafast free-carrier relaxation dynamics is carried out by fitting the fluence dependent recombination dynamics using the bi-exponential function, given by $\frac{\Delta E}{E}(t_p) = A_1 e^{\frac{t_p}{\tau_1}} + A_2 e^{\frac{t_p}{\tau_2}}$, where (τ_1 , τ_2), respectively represent the fast and slow relaxation time constants and (A_1 , A_2) are the probability amplitudes of the relaxation processes occurring in the photo-excited PbI₂ thin-film. All the fluence dependent differential transmission ($-|\Delta E/E|$) curves were simultaneously fitted by sharing the same slow recombination time constant (τ_2), as it does not depend on the fluence of the excitation pump pulse. The fast recombination time constants (τ_1) for the curves were extracted to be in the range of 12.76 ± 1.45 ps to 8.15 ± 0.56 ps, which show decreasing τ_1 with increase in the excitation pulse fluence (from $\Phi = 50 \mu\text{J cm}^{-2}$ to $400 \mu\text{J cm}^{-2}$). The fast relaxation (τ_1) in the PbI₂ thin-films is attributed to the trap assisted recombination processes that strongly depend the applied pump fluence (Φ) and the number of electrons relaxing from the conduction band-edge to the trap states. As the number of electrons is increased in the conduction band with the increasing pump fluence, results in the faster recombination (τ_1) due to the lesser available trap states. On the other hand, the slow relaxation (τ_2) is attributed to the electron-hole recombination from the trap states to the valance band maxima that shows ultrafast recombination time constant of $\tau_2 = 50.18 \pm 3.35$ ps. This value is in the similar range as the lifetimes measured for the PbI₂ nanoparticles and thermally evaporated films reported in the earlier studies.

Fig. 1(d) shows the fluence dependent transient photoconductivity ($\Delta\sigma(\tau_p)$) plots for the photoexcited 160 nm thin PbI₂ film, using the expression described in the Methods section. The photoconductivity was extracted from the fluence dependent corresponding $-\Delta E/E$ curves shown in Fig. 1(c), where their dependence is proportional. The photoconductivity increases with increasing pump fluence that shows linear variation below $\Phi = 400 \mu\text{J cm}^{-2}$, which defines the linear regime of the photo-excitation of the PbI₂ thin-film sample. For $\Phi > 400 \mu\text{J cm}^{-2}$, the photoconductivity deviates from the linear regime and eventually saturates at higher fluences. In the inset of Fig. 1(d), we plot the peak photoconductivity values with respect to the pump fluence that highlights the linear and saturation regime of the photo-induced change in conductivity. The free photo-carrier density (n_0) for various pump fluences, is estimated using the formula, $n_0 = \frac{2\Phi(1-e^{-\alpha d})}{dE_{\text{pump}}}$, where Φ is the pump fluence, $\alpha = 1.5 \times 10^5 \text{ cm}^{-1}$ is the linear absorption coefficient of PbI₂ at energy of the pump $E_{\text{pump}} = 3.09 \text{ eV}$ and $d = 160 \text{ nm}$ is the thickness of the PbI₂ film. The high value for the absorption coefficient of the PbI₂ thin-film yields photo-excited free carriers density in the order of $9 \times 10^{19} \text{ cm}^{-3}$ that falls in the low fluence/linear regime of the change in the conductivity of the sample. Hence, the observed ultrafast relaxation of photo-carriers in 50 ps is not influenced by the higher order/nonlinear (two-photon absorption) processes as the system falls in the low-density regime at the excitation fluence of $400 \mu\text{J cm}^{-2}$ ($n_0 = 9 \times 10^{19} \text{ cm}^{-3}$). Therefore, the overall relaxation lifetime estimated from globally fitting the fluence dependent transients is majorly governed by the trap assisted first order electron-hole recombination process that depends on the surface defects and the effects due to phonon assisted couplings in the semiconductor.

Ultrafast photo-switching of Fano resonance in the PbI₂ spin coated TASR metamaterial

In order to technologically explore the ultrafast relaxation dynamics of the free carriers in PbI₂ thin-film, we designed a photoactive semiconductor-metamaterial hybrid device, where the observed 50 ps time constant of the recombining photo-carriers in PbI₂ is utilized to actively switch the sharp resonance features in the metamaterial structure at the ultrafast time scales. The artistic representation of the device is shown in Fig. 2(a), where the PbI₂ molecules (possesses hexagonal structure preferring (001) crystal orientation parallel to the substrate plane^[52]) are spin coated in the form of a thin-film over a terahertz asymmetric split ring resonator (TASR)

metamaterial fabricated on a quartz substrate (we refer this as PbI_2 -TASR sample). The unit cell dimensions of the TASR metamaterial with the periodicity of $75\ \mu\text{m}$ is shown in the inset diagram of Fig. 2(a). The optical microscope images of the bare- PbI_2 (PbI_2 -TF) and PbI_2 thin-film spin-coated metamaterial (PbI_2 -TASR) samples are shown in Fig. 2(b) and (c), respectively. The PbI_2 thin film covers the entire metamaterial structure allowing it to uniformly influence the localized near-fields confined in the gaps of the TASR unit cell structures (details of the fabrication and the spin coating techniques are provided in the Methods Section).

In Fig. 3(a) and (b), we present the experimentally measured ultrafast modulation of the resonance features in the PbI_2 spin coated hybrid TASR resonators with 160 nm (PbI_2 -TASR-1) and 500 nm (PbI_2 -TASR-2) thin PbI_2 films, respectively (details are provided in the Experimental Methods). The THz transmission characteristics in the TASR metamaterial samples lead to mode hybridization^[3] of the low frequency (at 0.7 THz) anti-symmetric Fano resonance and a symmetric broad dipolar resonance appearing at the higher frequency (near 1 THz). The observed mode hybridization results from the Fano type of interference effects between the ‘bright’ (dipole mode) and ‘dark’ (due to structural asymmetry) modes appearing within the unit cell of the structure. Earlier studies^[6,7] have shown that excitation of Fano resonance results in a large enhancement of electric energy confined in the gaps of resonator structures that constitutes the localized plasmons and governs the strength of the Fano resonance feature. Upon spin coating the PbI_2 films ($d_{\text{PbI}_2} = 160\ \text{nm}$ and $500\ \text{nm}$) on the respective TASR resonators, which fill up the capacitive gaps (g) in the structures act as a photo-active element within the gaps. Upon the incidence of the optical pump beam of energy 3.09 eV ($\lambda = 400\ \text{nm}$), the free carriers of the photoexcited PbI_2 thin-film present in the resonators gaps alter the strength of confined electric fields (localized plasmons). This change results in the strong modulation of the resonance amplitudes of the Fano and dipole features of the hybrid device along with a minimal red shift in their respective bare resonance frequencies. The observed small frequency shift of the resonance is due to the change in the effective capacitance of the device with respect to change in the optical properties of the photo-excited PbI_2 thin-film present in the gaps of PbI_2 -TASR structures.

For PbI_2 spin coated samples (PbI_2 -TASR-1 and PbI_2 -TASR-2) the switching cycle of these resonances occurs in the ultrafast time scales of less than 150 ps, with the modulation depths for

Fano resonance reaching as high as unity (complete modulation). The ultrafast nature of the switching comes from the fast e-h recombination process ($\tau_2 \approx 50$ ps) in the photoexcited PbI₂ thin-film that reaches to its steady state nearly within 150 ps time scales (inset of Fig. 3(c)). The ultrafast modulation characteristics, are shown by the measured terahertz transmission spectra at different time instants of the pump-probe delay time (t_p) starting from the position, where the pump beam has not yet arrived ($t_p \leq 0$ ps) to the complete recovery (steady) state of the system ($t_p \sim 150$ ps). Before the optical excitation (at $t_p \leq 0$ ps) of the PbI₂ sample, the structure exhibits the strongest Fano and dipole resonances (black lines in Figs. 3(a) and (b)). Once the sample is photo-excited, the Fano resonance (near 0.65 THz) shows complete switch-off at $t_p = 6$ ps after the arrival of the optical pulse at the sample, where the photo-excitation of the PbI₂ is the maximum (red lines in Figs. 3(a) and (b)). At the same time dipole resonance (near 1 THz) shows the amplitude modulation of nearly 50%. Once the recombination of the photo-carriers in PbI₂ thin-film reaches the steady state equilibrium ($t_p \sim 150$ ps), both the Fano and the dipole resonance features are fully recovered to their original strengths, thereby showing profound and complete modulation of the Fano resonance feature of the metamaterial structure (orange lines in Figs. 3(a) and (b)). Here, the PbI₂-TASR-1 and PbI₂-TASR-2 samples are optically pumped with a fluence of $\Phi = 400 \mu\text{J cm}^{-2}$ and $900 \mu\text{J cm}^{-2}$, respectively. The depth of modulation is determined by using the expression, $M = (T_{np} - T_p)/T_{np}$, where T_{np} is the amplitude of Fano/dipole transmission resonances without the pump and T_p is the transmission amplitude under the influence of the optical pump (refer to the Supporting Information Fig. S3 for the details). In Fig. 3(c), experimentally measured modulation depths for the Fano and the dipole resonances as a function of pump-probe delay time (t_p) are plotted, where for Fano, the modulation depth reaches to $M_{\text{Fano}} = 1$, and for dipole, the maximum achieved modulation is $M_{\text{dipole}} = 0.51$. For the Fano resonance, the resonance switches off completely at $t_p = 6$ ps and shows relatively slow recovery during initial t_p with measured $M_{\text{Fano}} = 0.99$ after 15 ps (i.e. modulation changes by only 1%, where the photoconductivity of PbI₂ reduces almost to 45 % at 15 ps). For $t_p > 15$ ps, the Fano amplitude recovers exponentially and comes back to its full strength within $t_p \sim 150$ ps. This behavior is true for both PbI₂-TASR-1 with PbI₂ thickness of $d_{\text{PbI}_2} = 160$ nm and PbI₂-TASR-2 with $d_{\text{PbI}_2} = 500$ nm samples showing the ultrafast modulation of metamaterial resonances at their respective pump fluences. While on the other hand, recovery in the depth of modulation for dipole resonance follows the exponential behavior, which is in accordance with the relaxation

dynamics seen for the PbI₂ thin film (inset Fig. 3(c)). These differences in the nature of recovery for the modulation of Fano and dipole resonances are because of the strength of the confined electric fields at their respective resonance frequencies. The electric field at the Fano resonance frequency shows a very strong enhancement and is more sensitive to the external perturbation compared to the dipole fields. In Fig. 3(d), the confined fields for the Fano resonance are shown, where by tuning the conductivity of the PbI₂, the strength of the confined fields in the gaps is adequately controlled in the ultrafast time scales. The ultrafast modulation of Fano resonance amplitude is reflected in the ultrafast switch-off and recovery of the confined electric fields in the resonator gaps with respect to change in the conductivity of the PbI₂ thin-film. Since the fields are sensitive to the screening effect from the photoexcited electrons, the fields are annihilated when the conductivity of the film is high and reaches $\sigma_{\text{PbI}_2} = 1940 \text{ S m}^{-1}$ ($t_p = 6 \text{ ps}$). The fields only start to recover nearly after 30 ps, when the conductivity of the sample is reduced to $\sigma_{\text{PbI}_2} = 600 \text{ S m}^{-1}$, which also signify the threshold conductivity of the material in the gap to support the excitation of Fano resonance in the structure. Later the recovery of the confined fields shows exponential increase in its field strength and achieve its full strength within 150 ps, where the conductivity of the thin film reduces to 70 S m^{-1} (refer to Supplementary Figure 4 for the E -field plot with respect to change in conductivity). The electric fields are simulated using computer simulation technology (CST) microwave studio simulation software under the unit cell boundary condition offered by the frequency domain solver (more details on the simulations are provided in the Supplementary Information).

PbI₂ thin film thickness dependent modulation of Fano resonances

Alongside the ultrafast modulation of the Fano resonance spectra, we study the influence of pump fluences and thickness of the PbI₂ thin film on the depth of modulation (M) and sensitivity of the device. In Figs. 4(a)-(c), we present the pump fluence dependent spectra for the PbI₂-TASR samples for varying thicknesses of the PbI₂ thin films ($d_{\text{PbI}_2} = 160 \text{ nm}$, 500 nm and $2.5 \mu\text{m}$). The black curves in the respective plots represent the THz transmission spectrum through the bare TASR metamaterial in the absence of PbI₂ thin-film that shows the maximum strength in the Fano resonance and dipolar resonance features at low (0.75 THz) and high (1.1 THz) frequencies, respectively. Upon spin coating with the PbI₂ thin-films of varying thicknesses on the respective samples, the resonances show reduced amplitude and frequency red-shift due to

the change in the conductivity and dielectric constants in the vicinity of the resonators' near-fields. As the incident pump fluence is gradually increased, a small red shift in its resonance frequency is observed along with decrease in the amplitude of the Fano and the dipolar resonances that is reflected in increasing the modulation depths. The change in the amplitude modulation depths of the Fano and the dipole resonances for the samples with respect to pump fluences are shown in Fig. 4(d)-(f), where the modulation of Fano follows the exponential trend, while the dipole modulation shows the linear response. The observed exponential and the linear response in the modulation of the Fano and dipole resonances highlight the distinctive nature of the near-field responses of respective resonances in the metamaterial. The sensitive nature of the Fano enhanced resonant field to the external perturbations results in a steep variation in its resonant responses in the low fluence regime, whereas the dipole resonance being the fundamental mode of the structure shows a linear modulation with respect to the pump fluence (refer to the respective E -field plots with respect to pump fluence in the Supplementary Figure 5).

As shown in Fig. 4(c), for the PbI_2 -TASR-1 sample spin coated with $d_{\text{PbI}_2} = 160$ nm thin-film shows complete annihilation in the amplitude of Fano resonance with its absolute modulation depth reaching unity ($M_{\text{Fano}} = 1$) at $\Phi = 400 \mu\text{J cm}^{-2}$. The Fano modulation saturates at $\Phi = 100 \mu\text{J cm}^{-2}$ with modulation depth reaching $M_{\text{Fano}} \approx 0.99$. For PbI_2 -TASR-2 sample ($d_{\text{PbI}_2} = 500$ nm), the transmission spectra exhibit distinctive value of the modulation depths for a given pump fluence exhibiting higher saturation point at $\Phi = 400 \mu\text{J cm}^{-2}$. Complete modulation of the Fano resonance ($M_{\text{Fano}} = 1$) occurs at much higher fluence of $\Phi = 900 \mu\text{J cm}^{-2}$, as shown in Fig. 4(e). Similarly, for the PbI_2 -TASR-3 sample ($d_{\text{PbI}_2} = 2.5 \mu\text{m}$), the saturation is further delayed showing partial switch-off of Fano resonance with the maximum modulation depth reaching $M_{\text{Fano}} = 0.82$ at $\Phi = 900 \mu\text{J/cm}^2$, as shown in the Fig. 4(f). The change in depths of modulation (M) for Fano resonance with respect to pump fluence (Φ) is fitted with an exponential function, $M_{\text{Fano}} = e^{-\alpha\Phi}$ (where α is the rate constant and Φ is the fluence), whereas the linear change in dipole modulation is fitted using the linear function, $M_{\text{dipole}} = a + b\Phi$, where, a is the intercept and b is the slope of the linear fitting. The obtained rate constants (α) for Fano modulation are 0.028, 0.009 and 0.004 for PbI_2 -TASR-1, PbI_2 -TASR-2 and PbI_2 -TASR-3 respectively, which affirms that the sensitivity and the rate of modulation are better for the PbI_2 -TASR-1 sample with

a thinner PbI_2 film. The modulation depth for the dipole resonance in TASR-MM-1 reaches as high as $M_{\text{dipole}} = 0.5$ at $\Phi = 400 \mu\text{J cm}^{-2}$, whereas for TASR-MM-2 and TASR-MM-3, the maximum achieved modulation for dipole at $\Phi = 900 \mu\text{J cm}^{-2}$ is $M_{\text{dipole}} = 0.52$ and 0.28 , respectively. Although the change in the modulation depths for all three devices follow the linear curve, their respective slope decreases as 0.0012 , 0.0005 and 0.00025 for increasing thicknesses of the PbI_2 thin-films. The thickness dependent sensitivity and modulation of the metamaterial resonances are due to the changing strength of the interactions between the localized plasmons (strongly localized on the surface) with the photogenerated free carriers (within the optical penetration depth of PbI_2 material), as the thickness of the PbI_2 is varied. Hence, the photogenerated carriers in thinner PbI_2 sample will experience stronger interactions with the surface localized fields and hence results in their effective screening compared to thicker PbI_2 samples. These results affirm that modulation of metamaterial resonances depend on the thicknesses of the spin-coated PbI_2 thin-film, where the thinner films aid much sensitive modulation with low pump fluences.

Effect of trapped plasmons on the recombination lifetimes of the PbI_2 thin-film

Dependence of the resonance modulation on the thickness of the thin film material can be understood by looking at the t_p dependent differential THz transmission ($|\Delta E|$) through the PbI_2 -TASR samples with PbI_2 thin-films of thicknesses $d_{\text{PbI}_2} = 160 \text{ nm}$, 500 nm and $2.5 \mu\text{m}$. The differential transmission of the THz probe is defined as the $|\Delta E| = |E_{\text{nopump}} - E_{\text{pump}}|$. Fig. 5 presents the measured $-|\Delta E|$ of the THz probe with respect to the pump-probe delay times (t_p) for three different thicknesses of the PbI_2 thin-films (PbI_2 -TF) and thin-films spin coated on TASR metamaterial (PbI_2 -TASR) samples. For the bare thin-film (PbI_2 -TF) samples, $|\Delta E|$ of the THz probe depends on the number density of photoexcited free electrons on the surface of the thin-films that is dictated by their optical penetration depth. The optical penetration depth for the PbI_2 thin-film sample is nearly 64 nm at 400 nm optical wavelength. Upon photoexciting the thin-films, the surface conductivity of the sample increases within the optical penetration depth of the PbI_2 thin-film that in turn changes the $|\Delta E|$ of the THz through the sample. Fig. 5(a) shows the measured pump-probe time dependent $-|\Delta E|$ curves for the bare PbI_2 thin-film samples of different thicknesses, $d_{\text{PbI}_2} = 160 \text{ nm}$, 500 nm and $2.5 \mu\text{m}$. The measurements show identical $|\Delta E|$

response ($|\Delta E|_{\max} = 0.0032$) for all three thicknesses at $\Phi = 900 \mu\text{J}/\text{cm}^2$, which clearly indicates that the change in the THz transmission through the sample does not depend on its film thickness for bare PbI_2 -TF samples. This behavior is also true for other pump fluences, where PbI_2 -TF samples with different thicknesses show identical values in the measured $|\Delta E|_{\max}$, which increases with increasing Φ , as shown in the inset plot of Fig. 5(a). The proportionality of $|\Delta E|$ with Φ for the varying film thicknesses indicates the proportional change in their photoconductivity or number density, which in accordance with the previously discussed results for $d_{\text{PbI}_2} = 160 \text{ nm}$ thin-film sample in Fig. 1(d).

As the thin-films of different thicknesses are spin coated on the metamaterial structures (PbI_2 -TASR), the $|\Delta E|$ for the samples exhibit contrasting values for a given pump fluence, as shown in the Fig. 5(b). At $\Phi = 900 \mu\text{J cm}^{-2}$, the $|\Delta E|_{\max}$ observed for the PbI_2 -TASR samples is greater than the corresponding PbI_2 -TF samples with the same film thicknesses. This enhancement in $|\Delta E|$ through PbI_2 -TASR samples signifies that the surface photoconductivity of the PbI_2 thin-film is strongly altered in the influence of trapped plasmonic field in the gaps of the TASR metamaterial structures. In the processes of photodoping the spin coated PbI_2 thin-film, increase in the number density of free electrons in the thin-film surface strongly interact with the localized plasmons confined in the gaps of the TASR structure. Interactions between the localized plasmons and free electrons in photoexcited PbI_2 would result in screening of the near-fields, thereby modulating the strength of resonances in the metamaterial, as discussed in the earlier sections. In turn, these localized plasmon-electron interactions also influence the photoinduced optoelectronic properties of the thin-film material. In the Fig. 5(b), we elucidate the effect of localized plasmon-electron interactions on the photoconductive properties of the PbI_2 -TASR samples, where difference between the measured $|\Delta E|$ with respect to t_p for PbI_2 -TASR samples ($t_{\text{PbI}_2} = 160 \text{ nm}, 500 \text{ nm}$ and $2.5 \mu\text{m}$) are shown. Each PbI_2 -TASR sample with different PbI_2 thickness exhibits different $|\Delta E|_{\max}$, hence signifies the film thickness dependent change in the THz ($|\Delta E|$) transmission at $\Phi = 900 \mu\text{J cm}^{-2}$. For a given Φ , the PbI_2 -TASR-1 sample with PbI_2 thickness of 160 nm exhibits larger $|\Delta E|_{\max}$ compared to other thicknesses and hence it results in the sensitive and low fluence switch-off of the Fano resonance in the structure (as discussed in Fig. 4(a)). The thickness dependent $|\Delta E|$ for PbI_2 -TASR samples are due to the changing strength of the interactions between the localized plasmons (strongly localized on the surface) with the photogenerated free

carriers (within the optical penetration depth of PbI₂ material). As the thickness of the PbI₂ film is increased, interaction strength decreases between the free carriers in PbI₂ and the out-of-plane exponentially decaying surface localized plasmons of TASR. Hence, the photogenerated carriers in thinner PbI₂ (PbI₂-TASR-1) sample will experience stronger interactions with the surface localized fields and that results in its larger $|\Delta E|_{\max}$ compared to thicker PbI₂ samples (PbI₂-TASR-2 and PbI₂-TASR-3). As a consequence of reduced interactions between the localized plasmons and free electrons for increasing film thickness, the measured $|\Delta E|$ through the PbI₂-TASR-1, PbI₂-TASR-2 and PbI₂-TASR-3 samples show decreasing numbers in $|\Delta E|_{\max} = 0.0086$, 0.008 and 0.0043, respectively.

The effects of localized plasmons and surface free electrons interactions in the PbI₂-TASR samples are further investigated by studying the recombination dynamics of photoexcited PbI₂ in PbI₂-TF and PbI₂-TASR samples, as shown in Fig. 5(c) and (d). The recombination dynamics of the photoexcited carriers in bare PbI₂-TF samples show similar recombination time constants for varying thicknesses of the samples. The time constants are calculated from the biexponential fitting discussed equation 1, where the average time constant for the recombination process is obtained using the expression, $\tau = \frac{(A_1\tau_1 + A_2\tau_2)}{A_1 + A_2}$, here, A_1 and A_2 are the amplitude coefficients and τ_1 , τ_2 are the fast and slow recombination time constants, respectively. For the bare PbI₂-TF samples of thickness $d_{\text{PbI}_2} = 160$ nm, 500 nm and 2.5 μm , the recombination dynamics show similar decay constants and the average time constant (τ) are plotted in the inset figure 5(c), where the respective values in τ do not show any appreciable deviations from each other. The overall decrease in the τ with respect to the pump fluence (Φ) can be accounted for the increase in the free carrier density with increasing Φ , which would essentially decrease the recombination lifetimes due to multiparticle interactions. On the other hand, for the PbI₂-TASR samples, the recombination dynamics shown in Fig. 5(d) depict significant deviations in the values τ for the samples with different PbI₂ thicknesses. The PbI₂-TASR sample with thicker film ($d_{\text{PbI}_2} = 2.5$ μm) show relatively faster recombination dynamics compare to other samples spin coated with thinner films ($d_{\text{PbI}_2} = 160$ nm and 500 nm). In the inset of Fig. 5(d), variation of τ with respect to pump fluence (Φ) are plotted for PbI₂-TASR samples of $d_{\text{PbI}_2} = 160$ nm, 500 nm and 2.5 μm . The plot shows a consistent trend in the higher values in τ for the thinner sample ($d_{\text{PbI}_2} = 160$ nm)

than the thicker films, however at higher fluences ($\Phi > 400 \mu\text{J cm}^{-2}$) the deviation in the lifetimes becomes larger compared to that in the lower fluence regime. This indicates that due to the localized plasmons-electron interactions, the relaxation dynamics in the thin-film of PbI_2 show thickness dependence effect, which is absent in the bare thin-film ($\text{PbI}_2\text{-TF}$) samples.

To clearly elucidate the effects of localized plasmons and free electrons interactions on the recombination lifetimes, we look at the recombination dynamics for the $\text{PbI}_2\text{-TF}$ and $\text{PbI}_2\text{-TASR}$ samples having same PbI_2 film thickness. Figs. 6(a)-(c) present the fluence dependent average time constants (τ) of the relaxation of photoexcited free carriers for the $\text{PbI}_2\text{-TF}$ and $\text{PbI}_2\text{-TASR}$ samples of film thickness $d_{\text{PbI}_2} = 160 \text{ nm}$, 500 nm and $2.5 \mu\text{m}$, respectively. Time constants (τ) for the thin film in $\text{PbI}_2\text{-TASR}$ sample are faster than the bare thin-film ($\text{PbI}_2\text{-TF}$) sample for a given pump fluence. For $d_{\text{PbI}_2} = 160 \text{ nm}$ thin PbI_2 samples, the lifetimes are plotted till the fluence of $400 \mu\text{J cm}^{-2}$, where the due to the localized plasmon-free electron interactions the lifetimes in PbI_2 are modified in the $\text{PbI}_2\text{-TASR}$ samples that show faster response (Fig. 6(a)). Above $400 \mu\text{J cm}^{-2}$, where the localized plasmon fields are switched off in the $\text{PbI}_2\text{-TASR-1}$ ($d_{\text{PbI}_2} = 160 \text{ nm}$) sample, due to strong screening effect from the photoexcited free carriers. However, in the case of thicker PbI_2 samples, where the annihilation of localized fields happens at higher fluence, the average time constants of the free carrier recombination are shown up to $\Phi = 900 \mu\text{J cm}^{-2}$, as depicted in Figs. 6(b) and (c). The trend seen in the data clearly shows consistent lower numbers in the recombination time constants for PbI_2 in $\text{PbI}_2\text{-TASR}$ sample at higher film thicknesses. Further, with increasing fluence, the time constants are decreased for both the samples due to large number density of photo-carriers at higher fluences, which is in accordance with the earlier reports.

Discussion

Previous approaches on all optical switching in metamaterial-semiconductor hybrid systems so far have only shown the effects of increased free carrier density in semiconductor on the resonance features of metamaterial structures. It is revealed that the resonances show strong modulation in their amplitude and frequency due to the screening of the near-field energy by the photoexcited free carriers in the semiconductors. During this process there exists interactions between the surface localized plasmons of metamaterial and the photoexcited free carriers in the

semiconductor materials, which show strong influence on each other's optical characteristics. The current study reveals both these features in the PbI₂-TASR hybrid device, where the interaction between the localized plasmons and free electrons results in the ultrafast modulation of metamaterial resonances together with the modified relaxation dynamics and photoconductive properties of PbI₂ thin-film material. The enhancement in the material properties in the PbI₂-TASR samples is attributed to the interactions between the surface localized plasmons of metamaterial and the photoexcited free carriers in the semiconductor materials. These interactions can be quantified by the Purcell factors for the confined fields calculated using the expression, $P = \frac{3}{4\pi^2} \left(\frac{\lambda}{n}\right)^3 \left(\frac{Q}{V}\right)$, where λ is the wavelength, n is the refractive index of thin-film material, Q is the quality factor and V is the cavity volume. The Purcell factors for the TASR structure possessing Fano and dipole resonances are approximately equal to 1080 and 6 at $\lambda = 440 \text{ } \mu\text{m}$ and $300 \text{ } \mu\text{m}$ respectively, for refractive index ($n = 3.52$) of spin coated PbI₂ thin film (measured refractive index data for PbI₂ thin-film is provided in the Supplementary Information). The strong confinement of the resonant fields possessing high Purcell factors enhances the material properties such as recombination decay constants (τ) and the photoconductive nature of the photoexcited PbI₂ thin-film. Particularly, the optoelectronic properties, such as recombination dynamics and photo-responsive properties of the PbI₂ material are seen strongly dependent on the thickness of the PbI₂ thin-film spin coated on the metamaterial structures, which is uncharacteristic to the bare thin-film samples. The thickness dependence nature of the modified material properties in the hybrid PbI₂-TASR samples comes from the changing strength in the interaction between the spatially decaying localized plasmons and the photoexcited surface electrons in the material. Increasing the thickness of the PbI₂ film reduces the interaction strength between the surface electrons and the localized plasmons, thereby resulting in higher $|\Delta E|$ and τ for $d_{\text{PbI}_2} = 160 \text{ nm}$ and lower numbers for $d_{\text{PbI}_2} = 2.5 \text{ } \mu\text{m}$ in the PbI₂-TASR sample. Thus, reduced relaxation time constants for the thicker PbI₂ film in PbI₂-TASR sample result in the faster modulation of the resonance features in metamaterial, as depicted in Fig. 3(c). For instance at given $t_p = 23 \text{ ps}$ and 30 ps , modulation depths for the Fano resonance in PbI₂-TASR-2 ($d_{\text{PbI}_2} = 500 \text{ nm}$) are faster with $M_{\text{Fano}} = 0.794$ and 0.712 than in PbI₂-TASR-1 ($d_{\text{PbI}_2} = 500 \text{ nm}$) with $M_{\text{Fano}} = 0.935$ and 0.785 , respectively. Thus, by varying the thickness of the spin coated PbI₂ film, the ultrafast switching times of resonances can be tuned in real time, which provides a

novel platform to realize most-efficient, reusable, cost-effective, sensitive and real time tunable ultrafast all optical modulation of metamaterial resonances. With the benefit of unity modulation and the ultrafast response, the proposed PbI_2 spin coated metasurface gives a better switching efficiency and easy realization of tunable metasurfaces across the near- and far-infrared frequencies.

In summary, the ultrafast charge carrier dynamics of the solution processed PbI_2 thin-film were probed experimentally using time resolved terahertz spectroscopy. The strong photoconductivity and the ultrafast relaxation of charge carriers in photoexcited PbI_2 thin film was used to demonstrate the ultrafast switching and recovery of sharp Fano resonance feature in PbI_2 -TASR structure, where the complete switch-off ($M = 1$) and recovery of the Fano resonance feature is realized within ultrafast time scale of 150 ps. These results show an efficient, cost-effective and a simple spin-coating approach for realizing robust and ultrafast tunable metamaterial devices at the infrared and terahertz frequencies. Additionally, the localized plasmon and free electron interactions were revealed showing an enhanced photoconductivity and reduced relaxation time constants for the free carriers of photoexcited PbI_2 thin-film in the PbI_2 -TASR hybrid sample. These interactions are supported by the enhanced Purcell factors at Fano resonance frequency, which also revealed the thickness dependence of the modified material properties. Such plasmon enhanced interactions are beneficial for enhancing the photoinduced opto-electronic properties of the semiconducting material in designing ultrafast tunable photodetectors and modulators at near and far-infrared frequencies. Furthermore, with a greater significance and beneficial role of PbI_2 molecules in the prominent hybrid perovskite materials, the ultrafast carrier dynamics and the excellent photo-responsive properties of PbI_2 can provide new insights into the understanding of charge transport characteristics in developing high-efficient perovskite solar cells and ultrafast photodetectors.

Experimental methods

Sample fabrication. The lead iodide (PbI_2) thin film sample was prepared using the conventional solution-based fabrication protocol. The 500mg/ml ($d = 160$ nm) and 1000 mg/ml ($d = 340$ nm) PbI_2 (purchased from Acros Organics) was mixed in anhydrous DMF (Sigma Aldrich, 99.9%) and stirred at 70°C for two hours. Solutions were filtered with 0.45 μm polytetrafluoroethylene (PTFE) filter before spin coating on ASR-MD and quartz substrate at 4000 RPM for 30 seconds. Solvent engineering of these

films was performed by dripping 100 μ l toluene, 5 seconds after start of the spin-coating. Samples were subsequently annealed at 100 °C for 30 minutes. All the sample preparation and processing steps was performed in N₂ filled glovebox. AFM image of the spin-coated PbI₂ film is shown in the Fig. 1(a), which are obtained using the Asylum Research MFP-3D AFM system in the tapping mode.

The asymmetric split ring metamaterial (ASR-MM) sample consisting of $t_m = 200$ nm thick aluminum resonators was fabricated using the standard photolithography technique on a z-cut quartz substrate of thickness 1 mm. Quartz substrate was cleaned using acetone and IPA. After drying the substrate at 100 °C for 10 mins on a hot plate, a positive photoresist of thickness 1.5 μ m was coated on it. A positive mask that consists of resonators design was aligned on the photoresist on quartz substrate and was exposed to UV light after prebaking at 105° C. Later, it was soaked in a developer solution to develop the pattern. After patterning, 200 nm thick aluminum metal was deposited using thermal evaporation method and as a final step, it was soaked in acetone solution to liftoff the undesired aluminum to get the final metallic metamaterial structure, as shown by the optical microscope image in Fig. 2(b).

Time resolved terahertz spectroscopy (TRTS). The TRTS measurements were carried out using Optical-pump-Terahertz-probe (OTPT) setup that is based on ZnTe nonlinear THz generation and detection. Optical laser beam used for the generation of terahertz and for photo-excitation of the PbI₂ sample is derived from an amplifier laser system possessing pulse width of ~ 50 fs, pulse energy of 6 mJ at 800 nm with a 1 kHz repetition rate. The beam was split into two parts with one being used for pumping the ZnTe crystal for THz generation-detection and the other part of the beam was frequency doubled (400 nm, 3.09 eV) using a BBO crystal for optical excitation of PbI₂ thin film sample. The photo-excitation pulse has higher photon energy (3.09 eV) than the band gap of the PbI₂ sample, which is about 2.2 eV (563 nm). The optical pump beam has a beam diameter of approximately 5 mm, which is much larger than the focused terahertz beam spot size of nearly 4 mm at the sample position, providing uniform photo-excitation over the spin coated PbI₂ film. The time delay (t_p) between optical-pump and terahertz probe pulses was controlled by using a translational stage and the pump time delay for the terahertz modulation measurements in PbI₂ spin coated TASR is set to about $t_p = 6$ ps, where the photo-excited signal is the maximum. At this maximum pump signal, the terahertz scan was performed on the sample (PbI₂-TASR) and the reference substrate and later in the post processing steps the spectrum through the sample ($E_s(\omega)$) is normalized to the reference substrate transmission spectra ($E_R(\omega)$) using the relation $|T(\omega)| = |E_s(\omega)|/|E_R(\omega)|$.

Electric field simulations. The THz transmission response through the PbI₂-TASR metamaterial sample and the electric field distributions are numerically examined using the CST microwave studio Maxwell's

equation solver based on the finite differential time domain (FDTD) with unit cell boundary conditions. In the simulations, the aluminium metal of thickness 200 nm with DC conductivity, $\sigma_{DC} = 3.56 \times 10^7$ S/m was used to model metallic asymmetric split ring (TASR) metamaterial and the quartz with permittivity of 3.75 was chosen as the transparent substrate. On the top of the metallic structure 160 nm thick layer of material was placed and its optical property was defined by experimentally measured permittivity ($\epsilon_{PbI_2} = 13$) and photoconductivity of the PbI₂ layer at different excitation pump-probe delay times (t_p) and for various excitation pump fluences. The terahertz wave with the electric component of the field polarized perpendicular to the gap of TASR is incident in a normal angle on the designed metamaterial structure. The transmission response for TASR sample without the PbI₂ layer and PbI₂-TASR sample for varying photoconductivity of the PbI₂ layer is shown in the supplementary figure. Modulation in the Fano resonance (at 0.7 THz) is clearly seen for increasing pump-probe delay time and for increasing conductivity values (increasing pump fluences) that eventually disappears at the conductivity value of PbI₂ equal to 1940 S/m ($t_p = 6$ ps) and recover after 150 ps for the respective conductivity value of 70 S/m. The electric field distribution are calculated at the Fano and the dipole resonance frequencies for time varying conductivity of the PbI₂ thin film and the same are shown in Fig. 3(d) and in supplementary figure, respectively.

Transient photoconductivity calculation. The experimentally measured $-|\Delta E/E|$ are used to calculate the transient photoconductivity ($\Delta\sigma(t_p)$) of the sample using the following relation, given by,

$$\Delta\sigma(\omega) = -\frac{\epsilon_0 c}{d} (n_{air} + n_{sub}) \left| \frac{\Delta E}{E} \right|$$

Where, c is the speed of light, d is the thickness of PbI₂ thin film, n_{air} and n_{sub} are the refractive indices of air and substrate, respectively. E is terahertz transmission through film without optical pump and ΔE is the change in THz transmission in the presence of optical pump beam.

Acknowledgements

Authors thank Y. K. Srivastava for his kind and timely assistance on the photolithography fabrication process. M.M, A.K and R.S acknowledge the funding from Ministry of Education Academic Research Fund Tier 2 grants MOE2015-T2-2-103 and MOE2017-T2-1-110. A.S and T.C.S. acknowledges the financial support from the Ministry of Education Academic Research Fund Tier 1 grants RG101/15 and RG173/16, and Tier 2 grants MOE2015-T2-2-015 and MOE2016-T2-1-034; and from the Singapore National Research Foundation through the

Singapore–Berkeley Research Initiative for Sustainable Energy (SinBeRISE) CREATE Program and the Competitive Research Program NRF-CRP14-2014-03.

References

1. J. B. Pendry, A. J. Holden, D. J. Robbins, and W. J. Stewart. *IEEE Trans. Microwave Theory Tech.* **1999**, 47, 2075.
2. N. Engheta, and R. W Ziolkowski. *John Wiley & Sons*, 23 Jun **2006**.
3. V. A. Fedotov, M. Rose, S. L. Prosvirnin, N. Papasimakis, and N. I. Zheludev. *Phys. Rev. Lett.* **2007**, 99, 147401.
4. B. Luk'yanchuk, N. I. Zheludev, S. A. Maier, N. J. Halas, P. Nordlander, H. Giessen, C. T. Chong. *Nat. Mater.* **2010**, 9, 707-715.
5. A. E. Miroshnichenko, S. Flach, and Y. S. Kivshar. *Rev. Mod. Phys.* **2010**, 82, 2257-2298.
6. N. Liu, L. Langguth, T. Weiss, J. Kästel, M. Fleischhauer, T. Pfau, H. Giessen. *Nat. Mater.* **2009**, 8 (9), 758-762.
7. R. Singh, I. A. I. Al-Naib, M. Koch, and W. Zhang. *Optics Express*, **2011**, 19 (7), 6312-6319.
8. N. I. Zheludev, S. L. Prosvirnin, N. Papasimakis, and V. A. Fedotov. *Nat. Phot.* **2008**, 2, 351-354.
9. Y-W Huang, W T Chen, P C Wu, V. A. Fedotov, N. I. Zheludev and D. P. Tsai. *Sci Rep.* **2013**, **3**, 1237.
10. C. Wu, A. B. Khanikaev, R. Adato, N. Arju, A. Ali anik, H. Altug, and G. Shvets. *Nat. Mater.* **2012**, 11, 69–75.
11. N. Liu, T. Weiss, M. Mesch, L. Langguth, U. Eigenthaler, M. Hirscher, C. Sönnichsen, H. Giessen. *Nano lett.* **2009**, 10 (4), 1103-1107.
12. M. Gupta, Y. K Srivastava, M. Manjappa, R. Singh. *Appl. Phys. Lett.* **2017**, 110, 121108.
13. K. V. Sreekanth, Y. Alapan, M. ElKabbash, E. Ilker, M. Hinczewski, U. A. Gurkan, A. D. Luca and G. Strangi. *Nat. Mater.* **2016**, 15, 621–627.
14. T. Nakanishi, T. Otani, Y. Tamayama, and M. Kitano. *Phys. Rev. B* **2013**, 87, 161110(R).
15. M. Manjappa, Y. K. Srivastava and R. Singh. *Phys. Rev. B* **2016**, 94, 161103(R).
16. N. I. Zheludev and Y. S. Kivshar. *Nat. Mater.* **2012**, 11, 917-924.
17. W. Zhu, A. Liu, T. Bourouina, D. Tsai, J. Teng, X. Zhang, G. Lo, D. Kwong, and N. Zheludev. *Nat. commun.* **2012**, 3, 1274.

18. P. Pitchappa, M. Manjappa, C. P. Ho, R. Singh, N. Singh, C. Lee. *Adv. Opt. Mater.* **2016**, 4, 541–547.
19. M. Manjappa, P. Pitchappa, N. Singh, N. Wang, N. I Zheludev, C. Lee, and R. Singh, arXiv preprint **2018**, arXiv:1803.00594.
20. H. Tao, A. C. Strikwerda, K. Fan, W. J. Padilla, X. Zhang, R. D. Averitt. *Phys. Rev. Lett.* **2009**, 103 (14), 147401.
21. H-T. Chen, J. F. O'Hara, A. K. Azad, A. J. Taylor, R. D. Averitt, D. B. Shrekenhamer, and W. J. Padilla, *Nat. Photon.* **2008**, 2, 295–298.
22. M. Manjappa, Y. K. Srivastava, L. Cong, I. Al-Naib, and R. Singh. *Adv. Mater.* **2016**, 29 (3), 1603355.
23. M. R. Shcherbakov, S. Liu, V. V. Zubyuk, A. Vaskin, P. P. Vabishchevich, G. Keeler, T. Pertsch, T. V. Dolgova, I. Staude, I. Brener and A. A. Fedyanin. *Nat. Commun.* **2017**, 8, 17.
24. M. R. Shcherbakov, P. P. Vabishchevich, A. S. Shorokhov, K. E. Chong, D.-Y. Choi, I. Staude, A. E. Miroshnichenko, D. N. Neshev, A. A. Fedyanin, and Y. S. Kivshar. *Nano Lett.*, **2015**, 15 (10), 6985–6990.
25. S. H. Mousavi, I. Kholmanov, K. B. Alici, D. Purtseladze, N. Arju, K. Tatar, D. Y. Fozdar, J. W. Suk, Y. Hao, A. B. Khanikaev, R. S. Ruoff, and G. Shvets. *Nano Lett.*, **2013**, 13 (3), 1111–1117.
26. A. Minovich, J. Farnell, D. N. Neshev, I. McKerracher, F. Karouta, J. Tian, D. A. Powell, I. V. Shadrivov, H. H. Tan, C. Jagadish, and Y. S. Kivshar. *Appl. Phys. Lett.* **2012**, 100, 121113.
27. W. J. Padilla, A. J. Taylor, C. Highstrete, M. Lee, R. D. Averitt. *Phys. Rev. Lett.* **2006**, 96, 107401.
28. W. X. Lim, M. Manjappa, Y. K. Srivastava, L. Cong, A. Kumar, K. F. MacDonald, R. Singh, *Adv. Mater.* **2018**, 30, 1705331.
29. T. Driscoll, H-T. Kim, B-G. Chae, B-J. Kim, Y-W. Lee, N. M. Jokerst, S. Palit, D. R. Smith, M. D. Ventra, D. N. Basov. *Science* **2009**, 325 (5947), 1518-1521.
30. Q. Wang, E. T. F. Rogers, B. Gholipour, C.-M. Wang, G. Yuan, J. Teng and N. I. Zheludev. *Nat. Phot.* **2016**, 10, 60–65.
31. Y. K. Srivastava, A. Chaturvedi, M. Manjappa, A. Kumar, G. Dayal, C. Kloc, R. Singh. *Adv. Opt. Mater.* **2017**, 1700762. doi: 10.1002/adom.201700762.
32. S. A Veldhuis, P. P Boix, N. Yantara, M. Li, T. C. Sum, N. Mathews, S. G Mhaisalkar,. *Adv. Mater.*, **2016**, 28, 6804–6834.

33. Z. K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, R. H. Friend, *Nat. Nanotechnol.* **2014**, 9, 687.
34. G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, T. C. Sum, *Nat. Mater.* **2014**, 13, 476.
35. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, *Nano Lett.*, **2015**, 15 (6), 3692–3696.
36. M. Manjappa, Y. K. Srivastava, A. Solanki, A. Kumar, T. C. Sum, R. Singh, *Adv. Mater.* **2017**, 29, 1605881.
37. L. Cong, Y. K. Srivastava, A. Solanki, T. C. Sum, R. Singh, *ACS Photonics*, **2017**, 4 (7), 1595.
38. A. Chanana, X. Liu, C. Zhang, Z. V. Vardeny and A. Nahata, *Science Advances* **2018**, 4, 5.
39. L. Li, Y. Deng, C. Bao, Y. Fang, H. Wei, S. Tang, F. Zhang, J. Huang, *Adv. Opt. Mater.*, **2017**, 1700672. DOI: 10.1002/adom.201700672.
40. W. Zheng, R. Lin, Z. Zhang, Q. Liao, J. Liu and F. Huang, *Nanoscale*, **2017**, 9, 12718-12726.
41. L. Wang, C. McCleese, A. Kovalsky, Y. Zhao, and C. Burda. *J. Am. Chem. Soc.* **2014**, 136, 12205–12208.
42. T. J. Jacobsson, J-P. Correa-Baena, E. H. Anaraki, B. Philippe, S. D. Stranks, M. E. F. Bouduban, W. Tress, K. Schenk, J. Teuscher, J.-E. Moser, H. Rensmo, and A. Hagfeldt, *J. Am. Chem. Soc.* **2016**, 138, 10331–10343.
43. Y. C. Kim, N. J. Jeon, J. H. Noh, W. S. Yang, J. Seo, Jae S. Yun, A. Ho-Baillie, S. Huang, M. A. Green, J. Seidel, T. K. Ahn, and S. I. Seok. *Adv. Energy Mater.* **2016**, 6, 1502104.
44. J. R. Klein, O. Flender, M. Scholz, K. Oum and T. Lenzer. *Phys. Chem. Chem. Phys.*, **2016**, 18, 10800.
45. S. Roth and W.R. Willig, *Appl. Phys. Lett.*, **1971**, 18, 328.
46. K.S. Shah, P. Bennett, M. Klugeman, L. Moy, L. Cirignano, Y. Dmitriyev, M.R. Squillante, F. Olschner and W.W. Moses. *IEEE Transactions On Nuclear Science*, **1997**, 44, (3).
47. A. Sengupta, B. Jiang, K. C. Mandal, and J. Z. Zhang, *J. Phys. Chem. B*, **1999**, 103, 3128-3137.
48. C.-X. Sheng, Y. Zhai, E. Olejnik, C. Zhang, D. Sun, and Z.V. Vardeny. *Optical Materials Express*, **2015**, 5 (3), 530.
49. J. F. Condeles, R. C. Z. Lofrano, J. M. Rosolen, and M. Mulato. *Brazilian Journal of Physics*, **2006**, 36 (2A), 320-323.

50. L. M. Herz, *Annu. Rev. Phys. Chem.* **2016**, 67, 65–89.
51. C. L. Vorakiat, T. Salim, J. Kadro, M-T. Khuc, R. Haselsberger, L. Cheng, H. Xia, G. G. Gurzadyan, H. Su, Y. M. Lam, R. A. Marcus, M-E. M-Beyerle, E. E. M. Chia, *Nat. Commun.* **2015**, 6, 7903.
52. C.-G. Wu, C.-H. Chiang, Z.-L. Tseng, Md. K. Nazeeruddin, A. Hagfeldt and M. Grätzel, *Energy Environ. Sci.*, **2015**, 8, 2725-2733.
53. R. Singh, J. Xiong, A. K Azad, H. Yang, S. A Trugman, Q.X Jia, A. J Taylor, H.-T. Chen. *Nanophotonics*, **2012**, 1 (1), 117-123.

Figures

Figure 1. (a) Depicts the atomic force microscope (AFM) image of the lead iodide (PbI₂) thin film sample deposited on a quartz substrate. The color bar signifies the roughness of the sample, which is about 3.82 nm. (b) The measured X-ray diffraction (XRD) of the PbI₂ thin film showing the diffraction peaks of the lead and the iodide composites. The inset figure represents the plot

showing the thickness of PbI_2 film (approx. $d_{\text{PbI}_2} = 160$ nm) measured using the surface profilometry. (c) Fluence (Φ) dependent transient dynamics of the spin coated PbI_2 sample showing the optical excitation and relaxation of the photo carriers in the ultrafast time scales with the global fitting of the rate equations. (d) Transient photoconductivity of the photoexcited PbI_2 sample for varying pump fluences. The inset figure shows the peak transient conductivity values for increasing Φ that highlights the linear ($\Phi < 400 \mu\text{J cm}^{-2}$) and the nonlinear regime ($\Phi > 400 \mu\text{J cm}^{-2}$) of the photoconductivity in the photoexcited PbI_2 sample.

Figure 2. (a) Graphical representation of the PbI_2 spin coated TASR metamaterial (PbI_2 -TASR) design highlighting the pump-probe excitation of the sample along with its unit cell dimensions, length, $l = 60 \mu\text{m}$; width, $w = 6 \mu\text{m}$; asymmetry, $a = 15 \mu\text{m}$ and the capacitive gap, $g = 3 \mu\text{m}$. Periodicity of the structure is $75 \mu\text{m}$. (b) and (c) are respectively the optical microscope (OM)

images of the fabricated metamaterial sample without and with the spin coating of the PbI₂ thin film.

Figure 3. (a) and (b) THz transmission spectra of the PbI₂-TASR-1 and PbI₂-TASR-2 samples spin coated with the 160 nm and 500 nm thin PbI₂ films, measured at various pump probe delay (t_p). (c) Depicts the change in the modulation depths (M) of the measured Fano and the dipole resonance curves in (a and b) as a function of pump-probe delay time (t_p). The change in the modulation depths shows the ultrafast response that is in accordance with the measured ultrafast charge carrier dynamics of the PbI₂ thin film at $\Phi = 400 \mu\text{J/cm}^2$, as shown in the inset figure. (d)

Numerically extracted electric field strengths at the Fano resonance frequency (0.7 THz) for varying conductivity of PbI₂ showing the ultrafast switch-off and the recovery of the confined electric fields in the resonator gaps.

Figure 4. (a), (b) and (c) Experimentally measured THz transmission spectra of the PbI₂-TASR-1, PbI₂-TASR-2 and PbI₂-TASR-3, respectively spin coated with $d_{\text{PbI}_2} = 160$ nm, 500 nm and 2.5 μm thick PbI₂ films showing the amplitude modulation for varying fluences of incident pump beam of energy 3.1 eV. (d), (e) and (f) The corresponding amplitude modulation depths of Fano and the dipole resonances showing the maximum absolute modulation depth of $M_{\text{Fano}} = 1$ at $\Phi = 400$ $\mu\text{J/cm}^2$ for PbI₂-TASR-1 and $M_{\text{Fano}} = 1, 0.8$ at $\Phi = 900$ $\mu\text{J/cm}^2$ for PbI₂-TASR-2 and PbI₂-TASR-3, respectively. The variation in M for The Fano modulation is fitted with an exponential function, $M_{\text{Fano}} = e^{-\alpha\Phi}$, where α is rate-constant and is equal to 0.028, 0.009 and 0.004 for the PbI₂-TASR-1, PbI₂-TASR-2 and PbI₂-TASR-3, respectively. Variation in the modulation of dipole resonance for the metasurfaces shows a linear response with different slopes as depicted by the linear fitting function, $M_{\text{dipole}} = a + b\Phi$, where slope $b = 0.0012, 0.0005$ and 0.00025 for PbI₂-TASR-1, PbI₂-TASR-2 and PbI₂-TASR-3, respectively. The errors bars are extracted using the residual error calculation from the fitted data.

Figure 5. Transient differential ($-|\Delta E|$) THz transmission through the photoexcited different thicknesses of PbI_2 in (a) pristine thin-film ($\text{PbI}_2\text{-TF}$) and (b) spin coated $\text{PbI}_2\text{-TASR}$ samples measured using TRTS measurements. The insets in the respective plots show the peak value of the differential transmission of THz through $\text{PbI}_2\text{-TF}$ and $\text{PbI}_2\text{-TASR}$ samples of PbI_2 thickness $d_{\text{PbI}_2} = 160$ nm, 500 nm and 2500 nm for varying pump fluences. (c) and (d) Normalized transient differential transmission of THz probe for $\text{PbI}_2\text{-TF}$ and $\text{PbI}_2\text{-TASR}$ samples highlighting on the relaxation time of the photocarriers. The insets in (c) and (d) represents the averaged relaxation time constants of the photocarriers for increasing pump fluences for the

PbI₂-TF and PbI₂-TASR samples extracted using the bi-exponential fitting of the respective recombination curves.

Figure. 6 Averaged recombination time constants versus Φ for the PbI₂-TF and PbI₂-TASR for varying thicknesses of PbI₂ film (a) 160 nm, (b) 500 nm and (c) 2.5 μm . The error bars are calculated using the residual numbers from the fitting.