

Full paper

Graphene-mediated enhanced Raman scattering and coherent light lasing from CsPbI₃ perovskite nanorodsJung-Hye Kim^{a,1}, Quyet Van Le^{b,1}, Thang Phan Nguyen^c, Tae Hyung Lee^d, Ho Won Jang^d, Won Seok Yun^e, Soon Moon Jeong^f, JaeDong Lee^e, Soo Young Kim^{g,*}, Hyunmin Kim^{a,**}^a Division of Biotechnology, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, 42988, Republic of Korea^b Institute of Research and Development, Duy Tan University, Da Nang, 550000, Viet Nam^c Department of Chemical and Biological Engineering, Gachon University, Seongnam-si, 13120, Republic of Korea^d Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul, 08826, Republic of Korea^e Department of Emerging Materials Science, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, 42988, Republic of Korea^f Division of Energy Technology, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, 42988, Republic of Korea^g Department of Materials Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, Republic of Korea

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ABSTRACT

Graphene-enhanced Raman scattering has been studied as an optical technique related to the selective electron transfer from graphene to the valence band of the contacted molecule, inducing a pileup of electrons within the conduction band and a “photogating effect” for subsequently illuminated light. Herein, we studied the Raman spectroscopy of CsPbI₃ nanorods sandwiched between two layers of graphene, revealing that weak coherent lasing also occurs. The photoluminescence intensity of α -phase CsPbI₃ nanorods drastically decreased with increasing graphene coverage, particularly on the top, leading to Raman modes at the first (~ 241 and ~ 312 cm⁻¹) and second (~ 640 cm⁻¹) overtones of polymeric iodides, as well as at ~ 3492 cm⁻¹. First-principle calculations reveal that the ~ 3492 -cm⁻¹ mode originates from the stimulated coherent light emissions of the highly populated electrons accumulated in the CsPbI₃ conduction band, which form because of the electronic resonance induced in the Pb and I degenerate states.

1. Introduction

Graphene, a two-dimensional (2D) carbon allotrope, exhibits excellent mechanical, electrical, and optical properties and is being used to produce rigid and light car frames, as a chemical reaction catalyst, and even in inks [1–3]. Furthermore, upon the application of a voltage, graphene emits light in a manner similar to carbon nanotubes. However, its emission efficiency is very low [4]. Nevertheless, it has been suggested that graphene has high potential for use in the contact electrodes that drive the core photoelectrically active elements in light-emitting diodes, solar cells, and wearable devices. However, methods for its mass production must be developed [5–7]. In the contact mode, graphene improves the resolution of electron microscopes, mass-spectroscopy viability of biological cells, and scattering efficiency

of generated light [8–10]. With respect to the latter application, graphene-enhanced Raman scattering (GERS) was proposed to explain the sudden appearance of vibrational modes in the spectrum of rhodamine 6G cast on a graphene surface; these modes are otherwise buried in the fluorescence background [11]. GERS has since been observed in several organic dye molecules using graphene–dye hybrid systems, and the conjugation has been extended to 2D materials as well, with the signal enhancement factor being as high as 10^5 [12,13]. GERS can be employed not only to detect nonfluorescent molecules, but also to increase the charge density [14,15]. Chemically induced signal enhancement is possible via rapid charge transfer through the molecule/graphene interface. However, the reason for the quenching of the fluorescence background during GERS remains unknown.

Perovskites are compounds such as P[ZnT_{1–n}]O₃ and BaTiO₃ with a

Abbreviations: GERS, graphene-enhanced Raman scattering; AR, aspect ratio; XRD, X-ray diffraction.

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ligand-based ceramic structure composed of two metallic positive ions and a negative oxide ion (ABO_3). Their piezoelectric characteristics make them suitable for creating (or muffling) supersonic waves. Hence, they are used in sound filters, resonators, and sensors [16]. In 2009, researchers reported that organic lead halide perovskites (MPbX_3 ; M = organic, X = Cl, Br, I) can harvest sunlight with a conversion efficiency of 3.8%; this has since been increased to more than 20% through various morphological and physiochemical advancements [17]. Thus, the excellent optical properties of lead halides make them highly suitable for use in both photovoltaics and photodetectors, memristors, and light-emitting sources [18–27]. The optical properties of shape-controlled lead halide perovskites are ascribable to the excitons as well as the lifespan and evolution of the phonons and polarons generated. There have been reports on the use of Raman spectroscopy to analyze these phenomena [28,29].

The morphological control of lead halide perovskites is an area of active research, and it has been reported that one-dimensional (1D) linear structures are promising for driving the inner cavity of light-lasing sources [30–32]. In this study, we synthesized 1D CsPbI_3 nanorods using the seed-growth method and encapsulated them within a graphene “sandwich” to protect them against moisture and laser heating. Raman spectroscopy was performed to elucidate the phonon behavior of this graphene–perovskite–graphene structure, and Raman bands corresponding to the single (241 and 312 cm^{-1}) and double (640 cm^{-1}) overtones of the polymeric iodide chains were observed. Moreover, moderate-intensity, shape-dependent optical lasing was observed at 3492 cm^{-1} , which exhibited phase synchronism with one of the single overtones, in contrast to the other graphene-related combination and overtone bands (D + D’, 2D, and 2D’) located nearby. We believe this “Raman band” can be ascribed to the coherent light generation from the high density of electrons piled up in the conduction band in the lead iodide perovskite, owing to the photogating state allowed by the efficient supply of electrons from the graphene to the valence band of the perovskite.

2. Results and discussion

Fig. 1a shows the synthesis of the CsPbI_3 nanorods via the hot-injection method [33]. The Pb source was prepared by dissolving PbI_2 salt in oleic acid and oleylamine in the presence of 1-octadecene. The Cs source was prepared by forming a dispersion of Cs_2CO_3 and oleic acid in 1-octadecene. Upon the mixing of these two sources at 170°C , reddish CsPbI_3 nanodots formed instantaneously. The addition of a hexane/acetone antisolvent resulted in the phase transformation of CsPbI_3 from the α -phase (black) to the δ -phase (yellow). The hexane/acetone volume ratio had a determining effect on the size and geometry of the CsPbI_3 nanorods (Fig. S1). Fig. S2 shows that randomly shaped and sized CsPbI_3 microcrystals formed for hexane/acetone ratios of 15/1 and 6/1. However, highly uniform CsPbI_3 nanorods were obtained by reducing the hexane/acetone ratio to 3/1 and 3/2. The size distribution of the CsPbI_3 nanorods was determined (Fig. 1b). In the case of sample P1a10, most of the CsPbI_3 nanorods had lengths of 5–6 μm , and the highest aspect ratio (AR) was 4.5:1. Nanorods with a low AR are less susceptible to physical damage. However, an additional bimodal peak was observed for the nanorods with an AR of ~ 10 . The crystalline structure of the CsPbI_3 nanorods was determined using X-ray diffraction (XRD) analysis (Fig. S2), and the obtained spectra were compared with those of cubic (α -phase, black) and orthorhombic (δ -phase, yellow) perovskites; these are the primary structures of perovskite materials [34]. The XRD spectrum of the P1a10 perovskite nanorod matched well with that of the δ -phase CsPbI_3 (calculated), indicating that the α -phase mostly transformed into the δ -phase in the hexane/acetone mixture. Still, the XRD peak overlaps with the reference positions corresponding to α -phase are weakly observable, especially in case of larger rods. Fig. 1c shows a selected-area electron diffraction micrograph taken from the larger rods (inset picture), clearly demonstrating the cubic nature of the crystalline structure. In contrast, the transmission electron microscopy images in Fig. S3 show that the previously reported lattice constants ($a = 10.462$, $b = 4.799$, $c = 17.765\text{ \AA}$) of the smaller (a few micrometers or shorter in length) nanorods are similar to the measured d -spacings of the

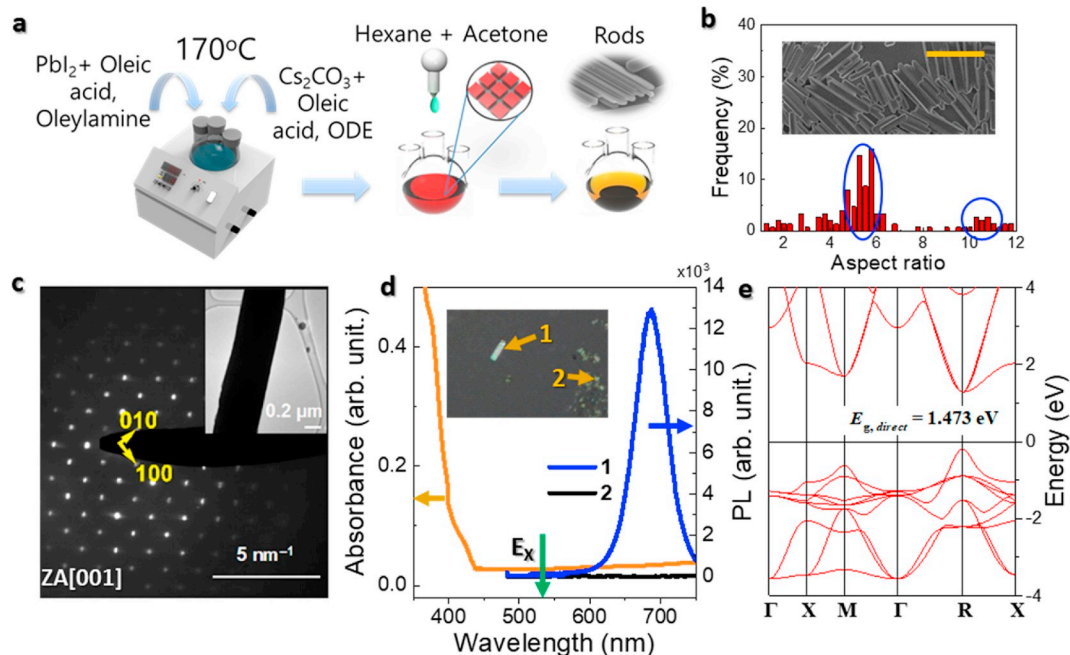


Fig. 1. CsPbI_3 perovskite nanorod synthesis and characterization. (a) Process for synthesizing CsPbI_3 nanorods. (b) Morphological characterization of CsPbI_3 rods. Inset: representative scanning electron microscopy image of the CsPbI_3 rods. The yellow scale bar is 5 μm . (c) Selected-area electron diffraction spectroscopy on α CsPbI_3 sample used in this work. Inset: transmission electron micrograph of the chosen rod. (d) UV–vis (orange) spectrum for the rod solution; photoluminescent spectra from the white rod (blue, mark 1) and yellow cluster (black, mark 2) in the inset image. E_x corresponds to the wavelength (532 nm) of the excitation beam for the Raman and PL spectroscopy. (e) Calculated electronic structure for the α -phase CsPbI_3 .

orthorhombic phase ($1/d_{\text{hkl}}^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$) [35]. The color change of the reaction solution (red to yellow; inset of Fig. S1b) indicates the phase conversion of the CsPbI₃ nanodots, and the positive number (higher than the tail of the absorption band of the red solution) in the absorption band (Fig. 1d) of the nanorods (orange line)—the arrow indicates E_x (532 nm)—is suggestive of the presence of α -phase. The photoluminescence of a white larger rod particle shows that there is a clear emission at 685 nm (1.81 eV, blue), whereas no light is generated from the yellowish clusters (black). Fig. 1e shows the calculated electronic structure of the α -phase CsPbI₃ unit cell and the symmetry points are shown in Fig. S4. The bandgap of the red α -phase CsPbI₃ nanorods is approximately 1.7–1.9 eV [36], which was quite well reproduced in the above experiments and theoretical calculations.

Fig. 2a shows a schematic of the graphene-sandwiched CsPbI₃ nanorods under laser illumination. In the case of gold nanorods coated with graphene, a high stress was induced in the nanorods, resulting in a phase shift in the Raman mode of the deposited graphene [37]. The illustration on the left in Fig. 2b shows the stepwise process for simultaneously depositing graphene on the top and bottom of the CsPbI₃ nanorods to form the graphene-sandwiched CsPbI₃ structure. The spin-casting process is also described in Fig. S1b. Thus, we could compare the light scattering from the CsPbI₃ nanorods irradiated by a 532-nm laser at 0.7 mW (at the sample) in the presence and absence of graphene. This is lower than the damage-free level (1.5 mW) reported in the literature [38]. It should be noted that the beam size was 2 μm according to the manual (Almeica XR, Nicolet). The fluorescence-like high-intensity luminance of the nanorods (green, marked as position 0) can be attributed to the defect-associated absorption, as explained in Fig. 1d. Similar to the case of GERS in organic dye molecules, the background was removed by the graphene at the bottom (marked as position 1) [11]. Further, Raman peaks were observed at ~ 241 and $\sim 312 \text{ cm}^{-1}$ in addition to a relatively broad peak at $\sim 640 \text{ cm}^{-1}$. A sharp

peak was seen at 3492 cm^{-1} , which was not related to any of the graphene-associated overtones or combination bands reported in the literature [39]. Moreover, the intensities of the GERS peaks of the CsPbI₃ nanorods in the case of the encapsulating (position 3) graphene were higher than those for the top (position 2) and bottom (position 1) graphene layers. Fig. 2c shows a magnified version of the GERS spectrum of the graphene-perovskite-graphene sandwich, which focuses on the lower- and higher-wavenumber regions. In addition to the two shoulder peaks at ~ 110 and $\sim 160 \text{ cm}^{-1}$ (attributable to the I–I vibrations in the I_3^- ions), two distinct peaks were seen at 241 and 312 cm^{-1} ; these are related to the overtone vibrational modes of the two shoulder peaks seen in the case of longer polymeric iodides [40]. Moreover, an additional Raman peak was seen at $\sim 640 \text{ cm}^{-1}$; this is probably the secondary overtone of the strong Raman emission at $\sim 320 \text{ cm}^{-1}$. In the case of the graphene-sandwiched perovskite, the Raman peak at $\sim 3492 \text{ cm}^{-1}$ was slightly redshifted (by $\sim 20 \text{ cm}^{-1}$), compared to that for the top-graphene-covered perovskite sample. It should be noted that this was the case in $\sim 15\%$ of all the measurements, presumably because the likelihood of the tension being relieved was greater in the case of the sandwiched structure [41]. The Q-factor ($f/\Delta f$, where f is the frequency) of this beam was obtained in a straightforward manner from the ratio of two wavenumber values by ~ 1000 ($\sim 15297/15$, where 15 is the Lorentzian full width at half maximum (FWHM)). The power-dependent Raman spectroscopy (Fig. 2d) was also monitored to more systematically assess the origin of the emission around 3942 cm^{-1} . From the figure, a potential appearance of the second node is vaguely noticed at 655 nm with the higher-fluence illumination, which was mostly overwhelmed by the broadband background in the 5-mW exposure induced by sample damage. The inset power-dependence profile was also evaluated to elucidate the GERS initiation point for a single nanorod sandwiched between two graphene layers, suggesting that a power level of $\sim 0.04 \text{ mW}$ was sufficient to initiate GERS with the signal-to-noise level

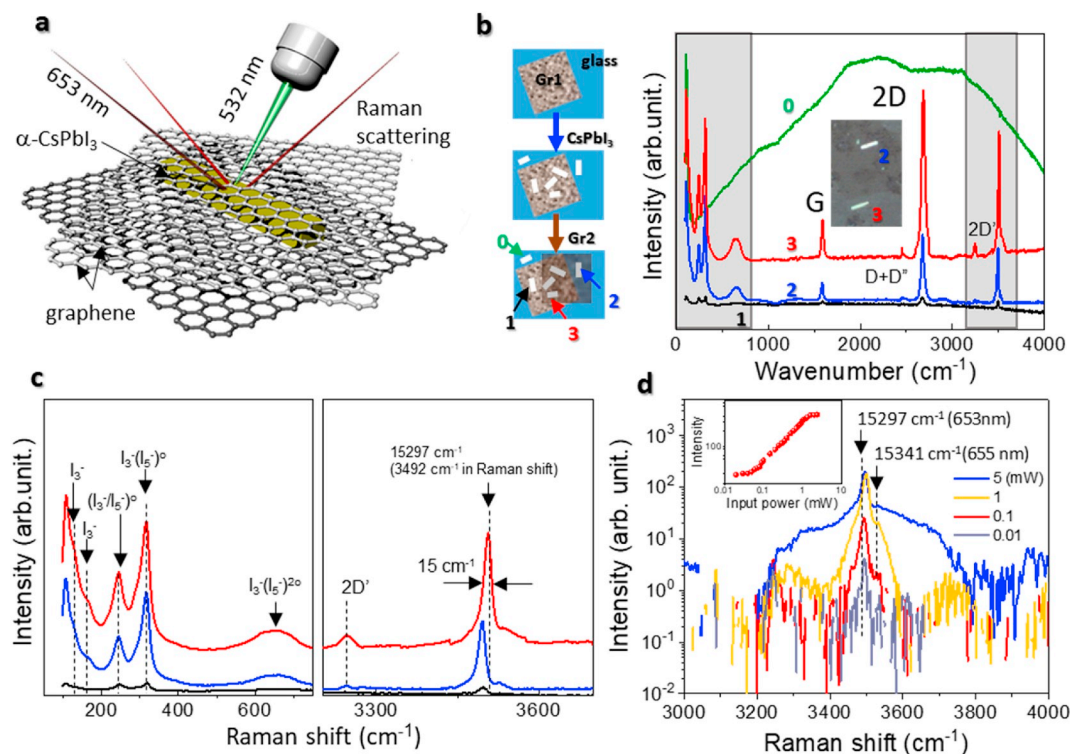


Fig. 2. Raman spectroscopy on the graphene-perovskite system. (a) Schematic of Raman scattering by CsPbI₃ nanorods sandwiched between single layers of graphene. (b) Raman spectra of CsPbI₃-graphene systems with different attachment geometries. Gr1 and Gr2 indicate the bottom and top graphene layers, respectively. The images on the left show the spectra responsible for the spectra shown on the right. Inset: optical microscopy image of the CsPbI₃ nanorods used for Raman spectroscopy. The yellow scale bar is 5 μm . (c) Magnified spectra corresponding to the low- and high-wavenumber regions marked in (b). (d) Power dependent Raman spectra of graphene-nanorod-graphene structure. Inset curve traced the Raman intensities at 3492 cm^{-1} as a function of excitation beam power.

of ~ 6 . To avoid considering any possible sample damage effects, measurements could only be performed at four power levels below 5 mW (at the sample). However, in spite of the limited range, the Raman intensity was found to be linearly dependent on the power level (slope = 1.03, $R^2 = 0.98$ in the case of the 3492 cm^{-1} peak). Nevertheless, it is clearly observable that the Raman intensity gradually diminishes under the higher-power lasing condition in the tail part of the inset “S” profile.

To elucidate the origins of the Raman peak at 3492 cm^{-1} in greater detail, we performed Raman mappings for five representative bands (241 , 312 , G, 2D, and 3492 cm^{-1}), as shown in Fig. 3.

Fig. 3a displays an optical micrograph of an arbitrary region of the graphene-sandwiched CsPbI₃ rods. We chose this region because the two nanorods in the image (labeled 1 and 2) had ARs of 5 and 10, respectively. Fig. 3b shows the Raman mapping for 241 cm^{-1} ; the direction of laser polarization is indicated by the double-sided red arrow. It was seen that nanorod 2 (AR = 10) exhibited a distinct two-edged emission when it was parallel to the direction of light polarization. In contrast, nanorod 1 (AR = 5) did not exhibit a strong emission under this condition. Moreover, the intensities of the Raman bands at 312 cm^{-1} (Figs. 3c) and 3492 cm^{-1} (Fig. 3d) were higher than those for nanorod 1. Meanwhile, in the case of the graphene peaks at 1680 cm^{-1} (G, Figs. 3e) and 2680 cm^{-1} (2D, Fig. 3f), the contrast between the two rods was significantly lower. In this sense, the emission at $\sim 3492\text{ cm}^{-1}$ coincided with that of the perovskite instead of that of the graphene, even though its Raman mode was closer to the high-wavenumber graphene-related overtone or combination band region ($2500\text{--}3300\text{ cm}^{-1}$) [42]. In addition, the relative intensity of the band at 3492 cm^{-1} , with respect to that of the 2D band, varied with the AR. Fig. 3g and h shows the Raman spectra of the thick (position 1; AR = 5) and thin (position 2; AR = 10) nanorods, respectively; the thickness of both nanorods was the same at 500 nm (see Fig. S5 for the characterization results). Given the beam polarization conditions, the spectra corresponding to positions 1 and 2 were similar, except that the Raman emission at $\sim 3492\text{ cm}^{-1}$ was higher than the 2D mode at position 1 and vice versa for position 2. For further clarity, we performed polarization-dependent Raman measurements by inserting a

half waveplate in the beam path. As can be seen from Fig. S5, the intensity of the Raman emission at 3492 cm^{-1} varied more for the thick CsPbI₃ nanorod than that for the thin nanorod. The polarization anisotropy (PA, $(I_{\max} - I_{\min})/(I_{\max} + 2I_{\min})$) of the 3500-cm^{-1} band of the thick nanorod was approximately 0.15 and increased to ~ 0.45 for the thin nanorod. It should also be noted that the PA values of the 241-cm^{-1} and 312-cm^{-1} bands were lower for the thick nanorod (~ 0.14 and ~ 0.43 , respectively) than those for the thin nanorod (~ 0.35 and ~ 0.67 , respectively) [43].

We also selected two thin vertically oriented CsPbI₃ nanorods (Fig. 4a) and analyzed their low-wavenumber vibrational modes in greater detail by performing Raman mapping (Fig. 4b and c). The beam polarization directions for rods i and ii were similar; however, the intensities of the Raman peaks at 241 and 312 cm^{-1} for nanorod i were almost an order of magnitude lower than those for nanorod ii.

This can also be confirmed from the magnified version of the left part of the spectrum, shown in Fig. 4d; the spectrum corresponding to the lower nanorod (red circle) was shown as a function of the beam polarization angle. When the direction of beam polarization (double-sided arrow) was at a right angle (10°) to the nanorod, the Raman intensities of the peaks at 241 and 312 cm^{-1} were similar (case i). However, when the beam polarization direction was almost parallel (rotated by 70°) to the nanorod, the intensities were different by approximately an order of magnitude (case ii). The complete polar plot for the three modes of interest (Fig. 4e) showed that the Raman peak at 241 cm^{-1} (black arrow) was shifted by $\sim 60^\circ$ with respect to those at ~ 312 (red arrow) and 3492 cm^{-1} (blue arrow) (Figs. S5g and S5h). The beam polarization direction dependency of the 640-cm^{-1} mode was close to that of the 312-cm^{-1} mode. Furthermore, this result suggested that the emission from the 3492-cm^{-1} mode was likely to be in-phase with that from the 312-cm^{-1} mode but not with that from the 241-cm^{-1} mode. It should be noted that the beam polarization direction dependencies of the two graphene-related Raman modes (G, green arrow, and 2D, pink arrow) were negligibly weak (Fig. 4f). The difference in the angles (54.7°) of the (111) and (100) crystal growth planes in the nanorod structure may

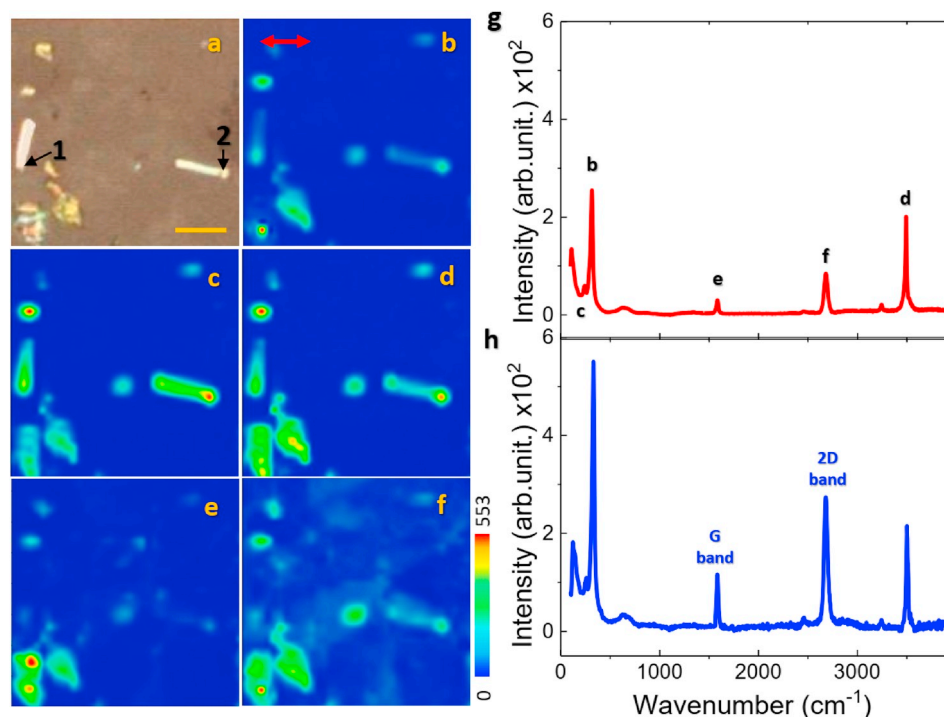


Fig. 3. Raman mode image mapping on graphene-perovskite-graphene structures. (a) Optical micrograph of random graphene-sandwiched CsPbI₃ nanorods and corresponding Raman intensity maps for peaks at (b) 241 cm^{-1} , (c) 312 cm^{-1} , and (d) 3492 cm^{-1} , and (e) G and (f) 2D bands. The yellow scale bar is $5\text{ }\mu\text{m}$. The red double-sided arrow represents the polarization direction of the excitation beam. Raman spectra of nanorods (g) 1 and (h) 2 marked in (a).

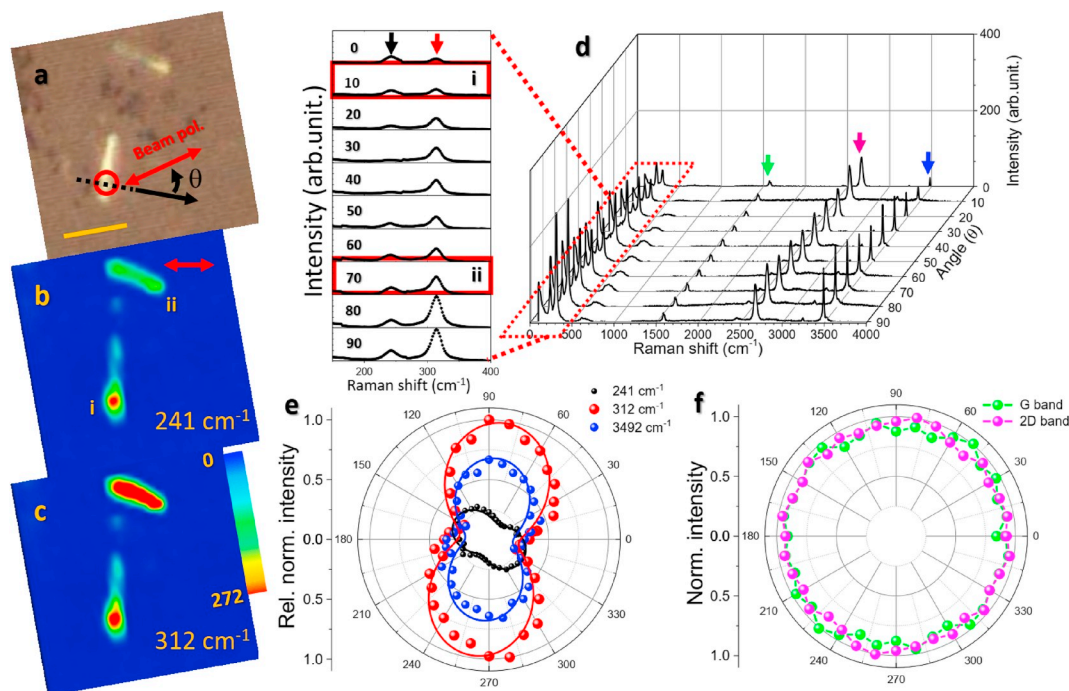


Fig. 4. Polarization-dependent Raman spectroscopy on graphene-perovskite-graphene structures. (a) Optical microscopy image of graphene-sandwiched CsPbI₃ nanorods and corresponding Raman maps for (b) 241- and (c) 312-cm⁻¹ modes. The yellow scale bar is 5 μm. The red double-sided arrow represents the polarization direction. (d) Raman spectrum of graphene-sandwiched CsPbI₃ nanorods as a function of the excitation beam polarization angle. The left side shows a magnified version of the Raman spectrum corresponding to the selected low-wavenumber region. Pole plots of Raman intensities of (e) 241-, 312-, and 3492-cm⁻¹ vibrational modes, and (f) 1590- and 2680-cm⁻¹ band modes.

explain the phase difference between the directions of the 241- and 312-cm⁻¹ modes of the polymeric chains.

To improve the understanding of light emission at the 3492-cm⁻¹ mode, we further analyzed the high-wavenumber region of the Raman spectrum by correlating the phenomena of momentum and energy transfer triggered by the excitation beam (532 nm) with the electronic structure of graphene (Fig. S6). The wave vector (1/532 nm⁻¹) induced by beam excitation is significantly smaller than those for electrons and holes; this results in an energy transfer instead of a momentum change. When the holes and electrons have been separated, their momenta can be transferred readily via the intra- (2D', pink) and intervalley (2D, yellow, or D + D', orange) transitions (Fig. 5a) [40]. To perform simulations under more realistic conditions, we constructed a graphene-perovskite interface composed of 7 layers of including 4 Cs, 3 Pb, and 12 I atoms attached to 24C atoms (Fig. 5b, Fig. S8). The calculated electronic structures of perovskite (blue) and graphene (red) are shown separately in Fig. 5c. In fact, the degenerate valence and conduction bands of the bulk perovskite are more realistic than those of the unit cell (Fig. 1d) and do not exhibit momentum-dispersive behavior. The locations of the possible defects are not specified but would be close to the band edges, given their role with respect to the changes in the momentum of the carriers [42]. Light from the excitation beam is preferentially absorbed by the perovskite nanorods, compared to graphene, owing to the former's superior absorption capability. This causes holes and electrons to recombine, resulting in Raman scattering (route 1) under fluorescence-muffled conditions, as in the case of graphene-organic dye systems [44].

On the contrary, light from the excitation beam can stimulate the emission of the densely populated electrons in the valence band of the perovskite under the defect-rich and fluorescence-muffled condition (route 2, Fig. 5e). The Q-factor of the lasing beam (~1000 in this case) is quite similar to that of the emission (1009) observed from the CsPbBr₃ nanorods, and the energy difference between the excitation beam (532 nm) and stimulated beam (653 nm) is analogous to the case between 400

and 530 nm in reference [45]; the rationale for the aforementioned suggestion is a Fabry-Pérot-type mechanism, which would be more clearly exhibited by the GERS effect in the presence of graphene. Fig. 5d shows the density of states drawn from the model in Fig. 5b. The transition corresponding to the 3492-cm⁻¹ mode is reminiscent of the electronically resonant transitions between van Hove singularities in semiconducting carbon nanotubes [46,47].

Alternatively or competitively, if the excited electron (2.33 eV) is allowed to transfer to a different reciprocal space in graphene (route 2') through the pseudo-intravalley transition (D'), the energy transfer back to the perovskite corresponding to the 3492-cm⁻¹ mode (0.43 eV) might be accomplished via a combination of sequential transitions, namely another D' transition and the 312-cm⁻¹ mode (0.04 eV). To summarize, the combination Raman band created by the mixing of the 2D' (3250-cm⁻¹, 0.40-eV) and 312-cm⁻¹ (0.04-eV) bands is close to the observed Raman mode at approximately 3500 cm⁻¹ (0.43 eV), with a slight loss in energy during the formation of the overtone (2D, 2D', and 2D'') and combination (D + D', D + D'', and D' + D'') bands in graphene. Nevertheless, regarding this issue, the most important point is the feasibility of the carrier momentum transfer between the graphene and perovskite. Several GERS studies have reported that hole transfers from graphene to the atomically thick organic dye layer (ms scale) [48] and quantum dots (s scale) [49] are rapid, whereas electron transfer in the reverse direction is restricted (ps and ns scale). Furthermore, the role of defects in a high number density within perovskites on the momentum transfer of electrons to graphene (unlike the graphene-only case) has not yet been clearly resolved.

3. Conclusions

We investigated Raman scattering by α-CsPbI₃ perovskite nanorods, whose fluorescence was quenched through contact with graphene. The all-inorganic CsPbI₃ nanorods were synthesized through the seed-growth method using CsPbI₃ quantum dots as the seeds. The GERS

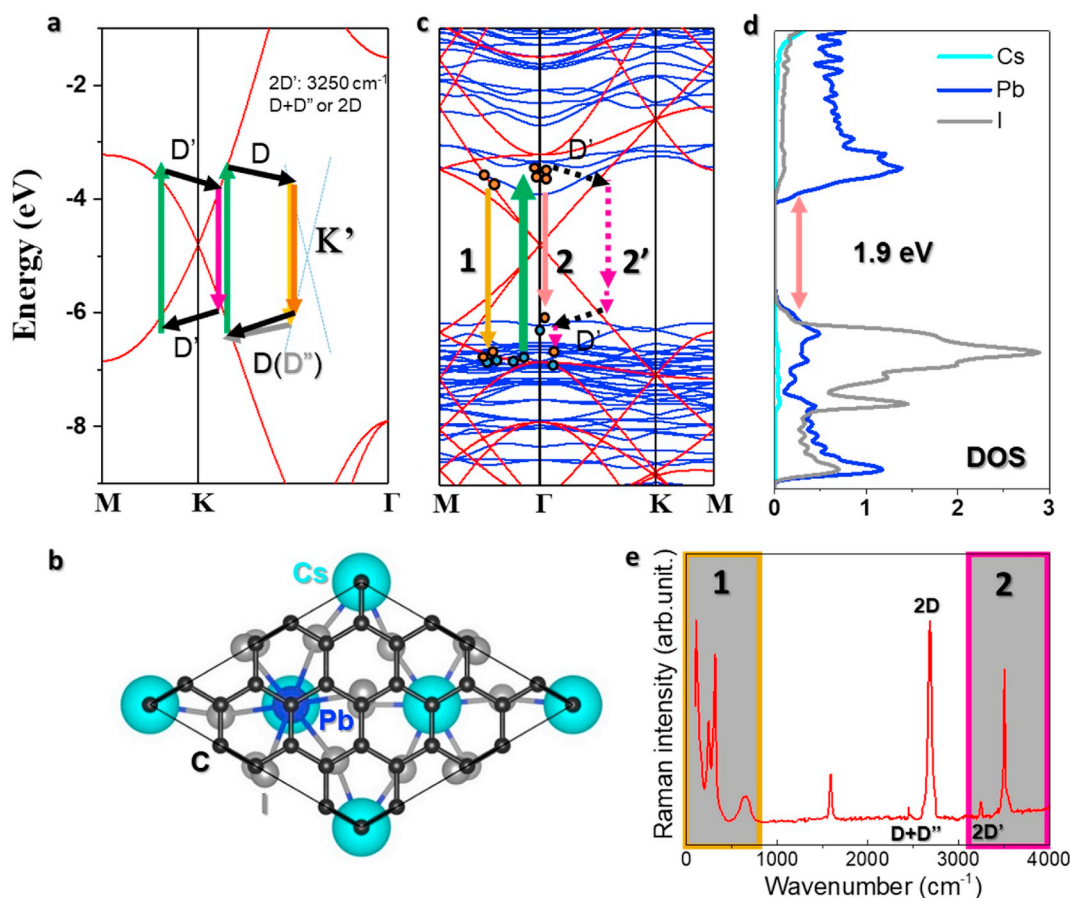


Fig. 5. Theoretical modeling on various light generations from graphene-perovskite systems. (a) $2D'$, $2D$, and $D + D''$ Raman modes defined in the electronic structure, calculated using rhomboid graphene unit cell shown in (b). (b) Top view of the calculation unit simultaneously containing $CdPbI_3$ and graphene. (c) Electronic structure and (d) density of states of $CsPbI_3$ -graphene hybrid system, calculated based on the red rectangle in (b). The orange and blue balls represent electrons and holes, respectively. (e) Representative Raman spectrum showing (1) the overtone spectra of iodide polymers and (2) the electronic pathway for the suggested combination band mode at 3492 cm^{-1} .

peaks observed at ~ 241 and 312 cm^{-1} correspond to the overtones of the Raman bands of the I_3^- structure and probably the cluster structures corresponding to the 110 - and 160-cm^{-1} bands, and were induced after excitation using a beam power of only 0.04 mW . The high scattering efficiency of the 312-cm^{-1} band resulted in another overtone mode, at $\sim 640\text{ cm}^{-1}$. Moreover, a new Raman-like emission was observed at 3492 cm^{-1} , whose intensity was higher than that of the $2D$ band of the thick nanorods ($AR \sim 5$), but lower than that of the $2D$ band of the thin nanorods ($AR \sim 10$). The phase of the 3500-cm^{-1} emission matched with that of the 312-cm^{-1} mode, but not with that of the 241-cm^{-1} mode when the polarization angle was changed by $\sim 60^\circ$. The first-principle calculations performed for graphene and the graphene- $CsPbI_3$ interface suggest that the emission from the 3492-cm^{-1} mode is similar to the Fabry-Pérot-type coherent emission with a Q-factor of 1000, and is related to the highly populated electron density in the lowest unoccupied molecular orbital of the perovskite system. It is also likely that this mechanism is aided by pseudo-van-Hove-singularity transitions from the I states in the valence bands to the Pb states in the conduction bands. Further future studies on the energy dispersion of electrons and molecular vibrations, with respect to different perovskites and $2D$ materials, should allow for controllability not only in the case of Fabry-Pérot-type, but also in the case of Raman-type lasers based on hybrid perovskite- $2D$ material heterosystems.

Author contributions

H.K. and S.Y.K. planned and supervised the project. Q.V.L. prepared

all the samples. J.-H.K., S.M.J., and H.K. conducted all the optical experiments; T.P.N., T.H.L., and H.W.J. performed the sample characterization. W.Y. and J.D.L. performed the theoretical calculations. J.-H.K., Q.V.L., H.K., and S.Y.K. analyzed the data and prepared the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary Information for this article can be found on the Nano Energy website (<https://www.journals.elsevier.com/nano-energy>).

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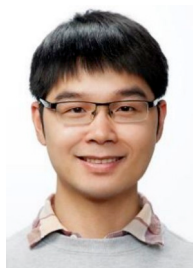
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