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Bandgap Control in Two-Dimensional Semiconductors via Coherent Doping of Plasmonic Hot Electrons

Teaser— *Using strong plasmon-exciton coupling to flexibly modify bandgap in two-dimensional semiconductors*

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Bandgap control is of central importance for semiconductor technologies. The traditional means of control is to dope the lattice chemically, electrically or optically with charge carriers. Here, we demonstrate for the first time a widely tunable bandgap (renormalisation up to 650 meV at room-temperature) in two-dimensional (2D) semiconductors by coherently doping the lattice with plasmonic hot electrons. In particular, we integrate tungsten-disulfide (WS₂) monolayers into a self-assembled plasmonic crystal, which enables coherent coupling between semiconductor excitons and plasmon resonances. Accompanying this process, the plasmon-induced hot electrons can repeatedly fill the WS₂ conduction band, leading to population inversion and a significant reconstruction in band structures and exciton relaxations. Our findings provide an innovative and effective measure to engineer optical responses of 2D semiconductors, allowing a great flexibility in design and optimisation of photonic and optoelectronic devices.

Introduction

Two-dimensional (2D) semiconductors, such as transition metal dichalcogenides (TMDCs)[1, 2], have direct bandgap at their monolayer limit, exhibiting tremendous potential in development of next-generation nanoscale devices. Like in their bulk counterparts, bandgap control plays a vital role in 2D semiconductor technologies, since it enables the creation of desirable optoelectronic properties that are required in numerous applications, ranging from lasers[3] to modulators[4], photodetectors[5] and photocatalysis[6]. The traditional means of control is to dope the lattice chemically[7], electrically[8] or optically[9] with charge carriers, the practicality of which is, however, limited by many factors, e.g. the irreversible bandgap modification, contact-type control and requirement of ultrastrong pump.

Here we report that one can effectively modify the electronic band structures of 2D semiconductors by establishing coherent strong coupling between the semiconductor excitons and a plasmonic resonator[10, 11]. In particular, plasmonic resonators are metallic nanostructures that support collective oscillation of electrons, known as plasmons. The excitation of plasmons can produce hot electrons, i.e. highly energetic electrons with non-equilibrium thermal distributions[12, 13], which, when plasmons are strongly coupled to 2D semiconductors, can repeatedly dope the lattice along with the coherent plasmon-exciton energy exchange. As a result, the bandgap of 2D semiconductors is significantly renormalised and the renormalisation can be easily altered via detuning plasmons from excitons.

Results

The schematic of our sample in Fig.1a demonstrates a WS₂ monolayer (ML) deposited onto a plasmonic crystal (PC)[14, 15], which comprises of a periodic array of silver capped silica nanospheres that are coated with an ultrathin Al₂O₃ spacer with a thickness of $t = 2.5 \pm 2$ nm. This metal-insulator-semiconductor configuration constitutes PC-WS₂ hybrid systems, supporting plasmon lattice modes propagating on the PC-WS₂ interface. Here the top WS₂ MLs belong to the family of atomically thin TMDCs, having been extensively studied[16–20] for their unusual exciton-dominated optical responses, such as high absorption and emission efficiency. These properties make the PC-WS₂ systems a suitable platform to study plasmon-exciton interactions[15].

The PC geometries were chosen to excite plasmon lattice modes[10, 11, 14, 15] that can match the frequency of exciton A ($E = 2.061$ eV) in WS₂ MLs at certain incident angles θ . Specifically, the plasmon modes show red-shift dispersion at higher θ (yellow curve in Fig.1b), which can be

FIG. 1. Structures of a PC-WS₂ sample and steady-state optical properties. **a**, schematic of polariton formation in a WS₂ ML that is supported on a self-assembled plasmonic crystal. The Al₂O₃ spacer is not depicted for simplicity. right insets: side and top-view scanning electron microscope (SEM) images; **b**, angle-resolved transmission spectra under p-polarised illumination and their projection (top x-y plane), in which the spectral positions of exciton A (X_A) and B (X_B), calculated dispersions of plasmon lattice modes (yellow curve), and upper and lower branches of polaritons (orange curves) are indicated. The tuned angle ($\theta = 22^\circ$) is marked with a black dashed line. Refer to Section 1 in the SI for detailed discussion of the strong plasmon-exciton coupling and its dispersion.

tuned in resonance with exciton A at $\theta = 22^\circ$. As the result, plasmon modes coherently couple with excitons, leading to the formation of plasmon-exciton polaritons, i.e. half-light half-matter quasi-particles that inherit properties from both the plasmonic and excitonic components. Such strong coupling presents as splitting transmission maxima that follow the dispersions of upper polariton (UP) and lower polariton (LP), and the hybrid system is characterised by a vacuum Rabi splitting of $\hbar \cdot \Omega_R \approx 136$ meV. More detailed analysis of strong plasmon-exciton coupling in equilibrium states can be found in a previous work[15] and Fig.S1 in the Supplementary Information (SI).

Upon photoexcitation by an optical pulse (3.1 eV and 100 fs), the transient optical responses of PC-WS₂ samples can be characterised using femtosecond transient absorption (TA) spectroscopy (Fig.2a and Methods), which enables incident angle-resolved probes of the system's relaxation dynamics[21]. Fig.2b shows the tuned state ($\theta = 22^\circ$) transient transmission spectra ($\Delta T/T$) under a pump fluence of $12 \mu\text{J}/\text{cm}^2$, in which the polaritonic system displays two split relaxation traces that flank the spectral position of exciton A, apparently corresponding to UP and LP. This ultrashort timescale result confirms again the strong coupling nature of the PC-WS₂ systems.

When the lattice plasmons are detuned from exciton A, e.g. at $\theta = 30^\circ$, the resonances red-shift to ~ 1.9 eV (Fig.S1 in SI). In this case, the transient spectra (Fig.2c) only show a single relaxation trace at 2.07 eV, which, by comparing with $\Delta T/T$ spectra of bare WS₂ MLs (Fig.S2 in SI), can be attributed to exciton A. However, no relaxation features from the detuned plasmons

are observed. We note that the plasmon features are also absent in $\Delta T/T$ of bare PCs (Fig.S13 in SI). As a previous study[22] pointed out, this is induced by the off-resonance frequency (3.1 eV) of the pump compared to the plasmon resonances, which results in very ineffective excitation of plasmons. These results indicate that the bare lattice plasmons can not be effectively excited without coupling to excitons under the pump conditions that can easily excite excitons.

FIG. 2. Transient optical responses of PC-WS₂ systems. **a**, schematic of angle-resolved ultrafast pump-probe spectroscopy; (note: the pump and probe beams are nearly colinear in practical experiments) **b**, **d** and **e** refer to normalised differential transmission spectra ($\Delta T/T$) at the tuned angle ($\theta = 22^\circ$), while **c**, **f** and **g** refer to $\Delta T/T$ at the detuned angle ($\theta = 30^\circ$); **b** and **c** are intensity plots of $\Delta T/T$ as function of time delay and probe photon energy, using the same colour bar (which is also used by Fig.3a); **d** and **g** are $\Delta T/T$ spectra averaged within the time span from 0.1 to 0.7 ps after pump; **e** and **f** are $\Delta T/T$ transient at specific energies (labelled with different colours), in which scatter symbols and solid curves represent measured and fitted data, respectively. Dashed frames in panel **b**, **d** and **g** mark the spectral region of the broad maxima (see main text). All measurements were carried out using 400 nm ($E = 3.1$ eV) pump pulses that have 100 fs duration and pump fluence of $12 \mu\text{J}/\text{cm}^2$ at room temperature. The instrument-response-function is shown as the grey area in panel **f**. All time axes are displayed in logarithmic scales.

What is interesting is that when the PC-WS₂ system is in tune (Fig.2b), there appears a $\Delta T/T$ maximum lasting for ~ 1 ps at the frequency range from $E = 1.6$ to 1.8 eV, which, in contrast, is remarkably weaker in the detuned state (Fig.2c) and is completely absent in bare WS₂ MLs (Fig.S2 in SI). From the integrated $\Delta T/T$ spectrum near zero probe delay (Fig.2d), we can see that the broad maximum has positive magnitudes, indicating negative optical absorption or positive gain, which sharply contrasts with the flat spectral features in not only the detuned polaritons (Fig.2g) but also the bare PC samples (Fig.S13 in SI).

FIG. 3. Transient optical responses under high-power pump. **a**, intensity plot of $\Delta T/T$ spectra of PC-WS₂ under $100\mu\text{J}/\text{cm}^2$ pump fluence at $\theta = 22^\circ$, where orange (blue) colour represents the maximum (minimum) value. **b**, delay time dependent spectra ($\Delta T/T$) at energies of UP, LP and exciton B extracted from panel **a**. Solid curves are plotted only for visual guidance **c**, $\Delta T/T$ spectra at different delay times, extracted from the white dashed frame in panel **a**; red dashed vertical line indicates the onset of renormalised bandgap. **d**, comparison of $\Delta T/T$ spectra at delay of 0.96 ps between PC-WS₂ (left) and WS₂ MLs (right) under gradually increasing pump fluence.

To confirm our observations, we have performed measurements under ~ 10 times higher pump fluence ($100\mu\text{J}/\text{cm}^2$) for the tuned polaritons (Fig. 3a), where the broad maxima are not only present but much more pronounced than the low-power case. In addition, we can see large spectral shift (Fig.S9) as well as remarkably delayed occurrence of UP and LP maxima (Fig.3b and Fig.S10), which indicate significant enhancement of the system's nonlinear optical responses (Details in Section 7 of SI). Similar to the low-power case, the transient variation of the broad maximum (Fig. 3c) takes ~ 1.5 ps from initial excitation to fading. Fig. 3d shows the development of the broad maxima upon pump fluence, where the magnitude and width of the maximum are highly dependent on pump intensity. Under $100\mu\text{J}/\text{cm}^2$ pump fluence, the full-width at half-maximum reaches at ~ 200 meV with highly enhanced magnitudes as compared to the maximum under $5\mu\text{J}/\text{cm}^2$ pump, also contrasting the flat spectral features in bare WS_2 MLs.

Discussions

According to previous works[9, 23, 24], the broad maxima are a clear evidence of bandgap renormalisation accompanied by population inversion, which is broadly understood as a population of high-density carriers in semiconductor lattice. In particular, when semiconductors are optically pumped, the generated non-equilibrium photo-carriers will occupy electron and/or hole states, leading to the formation of new quasiparticle bandgaps, which is described by[25]:

$$\Delta E_g = - \sum_{q \neq 0} V_s(q) [f_e(q) + f_h(q)] - \sum_{q \neq 0} [V_s(q) - V(q)] \quad (1)$$

where $V_s(q)$ and $V(q)$ represent fourier transforms of screened and unscreened Coulomb potentials, while $f_e(q)$ and $f_h(q)$ are occupation probabilities of electron and hole with momentum q . The onset of the new bandgap can be extracted from the low-energy end of the broad maximum. It means that in our experiments, the renormalised bandgap starts at $E_g \approx 1.60$ eV, lying ~ 400 meV below LP and ~ 650 meV below the initial bandgap of WS_2 MLs (given that the binding energy of exciton A is ~ 200 meV[19]).

These results, to the best of our knowledge, demonstrate the largest bandgap renormalisation in 2D semiconductors under such low pump intensities (e.g. down to $\sim 10 \mu\text{J}/\text{cm}^2$) to date. This sharply contrasts with similar observations[9] in bare WS_2 single/bi-layers with much stronger photoexcitation ($840\mu\text{J}/\text{cm}^2$ at 70 K or $3400\mu\text{J}/\text{cm}^2$ at room temperature). In their study, the ultrastrong pump enormously enhance exciton-exciton interactions, reducing exciton binding en-

ergy, finally breaking excitons into unbound electron-hole plasma. This effect is known as Mott-transition[9, 23], resulting in a high-density carrier population (up to $1 \times 10^{14} \text{ cm}^{-2}$) in WS_2 lattice. However, the pump power in our experiments is too low to develop a Mott-transition.

In addition, we note that the photoinduced absorption maxima (presenting as minima in negative $\Delta T/T$ magnitudes) in the tuned polaritons are clearly delayed as compared to its counterpart in the detuned polaritons (blue curves in Fig.2e and 2f and blue areas centred at $E = 1.95 \text{ eV}$ in Fig.2b and 2c). In bare TMDC MLs[17–19, 26], such postponed absorption maxima are usually observed under high-intensity pumps (e.g. Fig.S2c and Fig.S3 in SI), which, similar to Mott-transition, owes to enhanced exciton-exciton and/or exciton-electron interactions induced by high-power pump (see Section 2 & 6 in SI for detailed discussions). In contrast, the delayed maxima in our hybrid systems appear under much weaker pump and are only associated with the tuned polaritons. Together with the bandgap renormalisation, all these evidences suggest the presence of additional carriers that highly relate to the strong coupling.

In a coupled system, resonant energy transfer (RET) may enhance carrier population. Specifically, plasmons can resonantly transfer absorbed optical energy to excitons through dipole-dipole interaction, which can facilitate the generation of photo-carriers in semiconductors[27] (See Section 3 in SI for details). However, as explained before [Fig.2c, 2g and Fig.S13 (SI)], the plasmon modes cannot be directly excited by the off-resonance pump but can only be excited by coupling to excitons. In this case, the carrier density in lattice cannot be enhanced by plasmonic RET due to energy conservation.

We note that another source is more likely to contribute sufficient carriers, i.e. hot electrons from plasmonic crystals. Specifically, the excited plasmon modes may dephase from wave-like states through non-radiative decay, which generates electrons with non-equilibrium thermal distributions[13]. As a result, if plasmonic resonators are integrated with semiconductors, the excited electrons that have energies higher than the charge barrier formed at the metal-semiconductor interface can enter the lattice through direct electron transfer (DET)[28, 29], known as “hot electrons”. As the barrier can prevent charges from returning back to the metals[27, 28], hot electrons can dope adjacent semiconductors[30], modifying their photovoltaic and photocatalytic performance[12]. (See Section 3 in SI for details of DET)

It is worth noting that, similar to the previous study[22], in our PC- WS_2 systems the plasmonic hot electrons can only be generated through plasmon-exciton coupling. Specifically, after pumping, excitons in WS_2 MLs are first excited and then coherently exchange energy with plasmons

FIG. 4. **Hot electron density and distribution.** **a**, schematic illustration of the overall relaxation scenario after pulsed optical excitation on the PC-WS₂ systems, where the yellow oscillating dashed curve stands for repeated hot electron population in lattice; **b**, simulated intensity enhancement $|E/E_0|^2$ in a single sphere-cap unit (XZ cross-section at middle of the sphere) at the frequency of 2.05 eV, together with a schematic of the PC-WS₂ sample; please note that the WS₂ ML is partially suspended at interstices between two Ag caps, but not fully covering the metal surface; detailed morphology can be referred to our previous work[15]; **c**, calculated hot electron density along the curved WS₂ surface as a function of projected distance along x-direction (at the same cross-section as in panel **b**).

at the vacuum Rabi frequency ($\Omega_R \approx 136$ meV)[31]. As explained, the excitation of plasmons is accompanied by hot electron injection into the semiconductor. In other words, there is a fast and repeated hot electron population in the lattice that runs at an ultrashort period of ~ 30 fs ($T_R = 2\pi/\Omega_R$).

As shown in the schematic (Fig.4a), such an ultrafast electron population is not only shorter than the non-radiative decay (at scales of 10 ps) and the radiative decay process (up to few-hundred ps) in WS₂ MLs[17, 18], but also greatly shorter than the exciton formation (< 1 ps)[26]. This means that during exciton relaxation, hot electrons can repeatedly fill the unoccupied states in conduction band of WS₂ MLs. These injections can be evidenced by slower decays of both UP and LP (Fig.2e), compared with those of detuned states (Fig.2f and Table S2 in SI) and uncoupled excitons (Fig S2 and Table S1 in SI), because the electron population slows down the exciton bleaching via Pauli blocking and leads to extended lifetimes[22] (See Section 4 in SI for details).

The generated hot electron density in our system can be calculated from electric fields[32]. The near-field enhancement $|\mathbf{E}/\mathbf{E}_0|^2$ in our structure has been modelled and shown in Fig.4b, where $\mathbf{E}_0$ refers to the incident field and $\mathbf{E}$ stands for the enhanced field by plasmonic excitations. The field distributes along the Ag cap surface with hot spots at the interstices between caps. Starting with the Hamiltonians of an electron Fermi gas, we have developed a model to calculate the hot electron number N_e per unit area at the WS_2 surface (See Section 5 in SI for details):

$$N_e = \frac{1}{\pi} \frac{e^2 E_F^2}{\hbar} \frac{\hbar\omega - \Delta\phi_{\text{TB}}}{(\hbar\omega)^4} |\mathbf{E}_{\text{norm.}}|^2 \tau_{\text{pulse}} \quad (2)$$

where e is the electron charge, ω is the frequency, E_F is the Ag Fermi-level, $\mathbf{E}_{\text{norm.}}$ is the electric field normal to the surface and $\Delta\phi_{\text{TB}}$ is set to be 1 eV as the energy that is required to overcome the tunneling barrier formed at Ag- Al_2O_3 - WS_2 interface[29, 33]. As shown in Fig.4c, upon illumination by a pulse that has $12 \mu\text{J}/\text{cm}^2$ fluence and $\tau_{\text{pulse}} = 100$ fs duration (mimicking experimental conditions), along the WS_2 surface, the density of electrons that are capable of overcoming the tunneling barrier is typically higher than $1 \times 10^{13} \text{ cm}^{-2}$ with maxima values approaching $1 \times 10^{15} \text{ cm}^{-2}$ at the cap interstices.

It is noted that some losses were not included in this calculation, e.g. energy dissipation during photoexcitation, exciton formation and exciton-to-plasmon transfer process. In addition, it is very hard to obtain the ratio of the generated hot electrons that enter WS_2 lattice, because the current charge transfer models all build on phenomenological description, making the simulation tremendously complicated[34]. However, we note that the level of generated density is significantly higher than what is required to induce a large bandgap renormalisation. For example, the complete development of a Mott-transition in a WS_2 monolayer only requires a carrier density up to $1 \times 10^{14} \text{ cm}^{-2}$ [9]. In addition, a recent work[24] theoretically demonstrates that a charge doping density of $3.2 \times 10^{13} \text{ cm}^{-2}$ in WS_2 monolayers can already lead to a bandgap redshift up to 500 meV with carriers draining from conduction band K to Σ valley[35] that renders the semiconductor indirect. These results share high similarity with our observation, suggesting that even if only a small portion (e.g. $1/100 - 1/10$) of the generated hot electrons dope the lattice, one can observe the large bandgap restructuring as in our experiments.

Given that there is little evidence for other possible carrier sources, e.g. polariton condensates [36], we conclude that coherent doping of plasmonic hot electrons is dominantly responsible for the spectral and transient features that require high-density population. In particular, the hot

electron population starts with exciton formation and repeatedly takes place throughout the whole relaxation process. Owing to the existence of the tunneling barrier, hot electrons can be accumulated in the lattice before they decay (within 1 ps[13]), which simultaneously competes with rapid exciton relaxations, transiently converting the intrinsic WS₂ monolayers to “*n*-doped” ones. This leads to the giant bandgap renormalisation with population inversion that peak at few-hundred femtoseconds (Fig.2b, Fig.3c and Fig.S11 in SI), and also induces the delayed maxima in Fig.2b and 2e (see Section 6 in SI for details). When we enhance pump power, the hot electron density is accordingly increased, even capable of delaying the occurrence of excitation bleaching (Fig.3b and Fig.S10 in SI).

Summary

As discussed above, the strong plasmon-exciton coupling dramatically modifies the electronic band structures of WS₂ monolayers, which are induced, to a large degree, by plasmonic hot electron doping via strong coupling. This effect is extremely hard to observe in traditional exciton-polaritons[36], being a non-trivial factor that has to be considered when studying light-matter interactions using plasmonic resonators, which, on the other hand, provides new and effective measures to engineer bandgap of 2D semiconductors.

METHODS

1. sample preparation

Plasmonic crystals were prepared by self-assembly techniques together with thermal evaporation. In particular, silica spheres with diameter of 425 nm were self-assembled to a hexagonally packed monolayer on quartz substrates using a reported method[14], which is followed consecutively by evaporation of 40 ± 5 nm thick silver film and 2.5 ± 2 nm thick Al_2O_3 film. The metal evaporation acquires the shape of semi-spheres, resulting in an array of silver caps with a hexagonal lattice.

WS_2 monolayers were prepared using chemical vapour evaporation with sulfur powder and tungsten dioxide powder being precursors, respectively. Using the poly(methyl methacrylate)-assisted transfer method[37], we can transfer the prepared WS_2 monolayer onto the PC surface. It is noted that the presence of WS_2 monolayers is hardly seen from SEM images of our sample due to the ultrathin thickness of the monolayer (< 1 nm). For more details about the fabrication and the monolayer morphology of the PC- WS_2 samples please see our previous publication[15].

2. optical characterisation

The large sample areas ($2 - 4 \text{ cm}^2$) allow us to conveniently perform femtosecond pump-probe absorption measurements[38] with different incident angles. Specifically, as shown in Fig.2a, the PC- WS_2 samples were excited by a pump pulse, followed by a delayed broadband illumination to probe the photoexcitation induced changes, which can be characterised by measuring the differential transmission, defined as the normalised change of the probe transmission induced by the pump $\Delta T/T = (T - T_0)/T$, at different delayed times. The spectrometer in the pump-probe set-up is composed of a camera and a spectrograph, while the spectrograph is a home-built device using a prism to disperse the incident probe beam. The pump pulse has a frequency of 3.1 eV (400 nm), much higher than exciton A (2.061 eV), while the probe pulse has a broadband frequency from 0.5 to 2.5 eV. The whole ultrafast system acquires a pulse resolution of 100 fs, and were converted to p-polarisation (electric field parallel to the plane of incidence) before entering samples. The transmission spectra of PC- WS_2 samples in equilibrium states (without photoexcitation) were preformed using the reported method[15]. All optical characterisations were carried out at room temperature.

Supplementary Information

Section 1. Strong Coupling of Plasmons and Excitons

Section 2. Transient Optical Properties of WS₂ monolayers

Section 3. Strong coupling induced charge transfer and generation

Section 4. Transient Analysis of Plasmon-Exciton Polaritons

Section 5. Theoretical Model of Hot Electrons in plasmonic crystal

Section 6. Delayed Photoinduced Absorption with Polaritons

Section 7. Nonlinear responses

Section 8. Additional Transient Absorption Spectra

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Figures

Figure 1

Structures of a PC-WS2 sample and steady-state optical properties. a, schematic of polariton formation in a WS2 ML that is supported on a self-assembled plasmonic crystal. The Al₂O₃ spacer is not depicted for simplicity. right insets: side and top-view scanning electron microscope (SEM) images; b, angle-resolved transmission spectra under p-polarised illumination and their projection (top x-y plane), in which the spectral positions of exciton A (X_A) and B (X_B), calculated dispersions of plasmon lattice modes (yellow curve), and upper and lower branches of polaritons (orange curves) are indicated. The tuned angle ($\theta = 22^\circ$) is marked with a black dashed line. Refer to Section 1 in the SI for detailed discussion of the strong plasmon-exciton coupling and its dispersion.

Figure 2

Transient optical responses of PC-WS2 systems. a, schematic of angle-resolved ultrafast pump-probe spectroscopy; (note: the pump and probe beams are nearly colinear in practical experiments) b, d and e refer to normalised differential transmission spectra ($T=T$) at the tuned angle ($\theta = 22^\circ$), while c, f and g refer to $T=T$ at the detuned angle ($\theta = 30^\circ$); b and c are intensity plots of $T=T$ as function of time delay and probe photon energy, using the same colour bar (which is also used by Fig.3a); d and g are $T=T$ spectra averaged within the time span from 0.1 to 0.7 ps after pump; e and f are $T=T$ transient at specific energies (labelled with different colours), in which scatter symbols and solid curves represent measured and fitted data, respectively. Dashed frames in panel b, d and g mark the spectral region of the broad maxima (see main text). All measurements were carried out using 400 nm ($E = 3:1$ eV) pump pulses that have 100 fs duration and pump fluence of 12 $\mu\text{J}/\text{cm}^2$ at room temperature. The instrument-response-function is shown as the grey area in panel f. All time axes are displayed in logarithmic scales.

Figure 3

Transient optical responses under high-power pump. a, intensity plot of T=T spectra of PCWS2 under 100 $\mu\text{J}/\text{cm}^2$ pump fluence at $\theta = 22^\circ$, where orange (blue) colour represents the maximum (minimum) value. b, delay time dependent spectra (T=T) at energies of UP, LP and exciton B extracted from panel a. Solid curves are plotted only for visual guidance c, T=T spectra at different delay times, extracted from the white dashed frame in panel a; red dashed vertical line indicates the onset of renormalised bandgap. d, comparison of T=T spectra at delay of 0.96 ps between PC-WS₂ (left) and WS₂ MLs (right) under gradually increasing pump fluence.

Figure 4

Hot electron density and distribution. a, schematic illustration of the overall relaxation scenario after pulsed optical excitation on the PC-WS2 systems, where the yellow oscillating dashed curve stands for repeated hot electron population in lattice; b, simulated intensity enhancement $|E/E_0|^2$ in a single spherecap unit (XZ cross-section at middle of the sphere) at the frequency of 2.05 eV, together with a schematic of the PC-WS2 sample; please note that the WS2 ML is partially suspended at interstices between two Ag caps, but not fully covering the metal surface; detailed morphology can be referred to our previous work[15]; c, calculated hot electron density along the curved WS2 surface as a function of projected distance along x-direction (at the same cross-section as in panel b).

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