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Plasmonic Hot Carriers Controlled Second Harmonic Generation in WSe₂ Bilayers

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Abstract

Modulating second harmonic generation (SHG) by a static electrical field through either electric-field-induced SHG or charge-induced SHG has been well documented. Nonetheless, it is essential to develop ability to dynamically control and manipulate the nonlinear properties, preferably at high speed. Plasmonic hot carriers can be resonantly excited in metal nanoparticles and then injected into semiconductors within 10-100 fs, where they eventually decay on a comparable time scale. This allows one to rapidly manipulate all kinds of characteristics of semiconductors, including their nonlinear properties. Here we demonstrate that plasmonically generated hot electrons can be injected from plasmonic nanostructure into bilayer (2L) tungsten diselenide (WSe_2), breaking the material inversion symmetry and thus inducing an SHG. With a set of pump-probe experiments we confirm that it is the dynamic separation electric field resulting from the hot carrier injection (rather than a simple optical field enhancement) that is the cause of SHG. Transient absorption measurement further substantiate the plasmonic hot electrons injection and allow us to measure rise time of ~ 120 fs and fall time of 1.9 ps. Our study creates opportunity for the ultrafast all-optical control of SHG in an all-optical manner that may enable a variety of applications.

Keywords: plasmonic hot carrier injection, bilayer transitional metal dichalcogenides, inversion symmetry, charge induced second harmonic generation, transient absorption spectroscopy

The nonlinear optics on the nanoscale regime has attracted a lot attention in the last few decades¹⁻⁵. The nonlinear optics in nanoscale provides a host of fascination phenomena, which are remarkably useful in physics, biology and material science including advanced spectroscopy⁶, materials analysis⁷ and sensors^{8,9}. Dynamic control of the light signal is highly desired in the application of nonlinear optics. It has been proven that a static electric can be applied to a centrosymmetric material, and thus to induce and tune the SHG¹⁰⁻¹⁵, which was named as electric-field-induced second harmonic (EFISH). In addition, charge induced second harmonic generation (CHISHG) was demonstrated in transition metal dichalcogenides (TMDs) due to the charge accumulation¹⁰. From the theoretical point of view, second-order nonlinearity is not allowed within the electric-dipole approximation in a centrosymmetric medium. However, an external perturbation such as electric field can break that symmetry and induce substantial second-order nonlinearity¹⁶. For instance, the SHG of calcite bulk crystal can be enhanced significantly in the presence of a large static electric field¹³, a similar effect has been observed in the metal surface immersed in electrolytic solution¹⁴. EFISH can be formally described through third-order nonlinear susceptibility $\chi^{(3)}(2\omega, \omega, \omega, 0)$, *i.e.*, as a mixing between the static electric field and two optical fields.

While EFISH shows efficient control of SHG by applied voltage, this control cannot occur on an ultrafast scale as the required voltages are typically high and at high operating frequency the currents become unsustainable. For the wide band applications¹⁷, it is desirable to manipulate the SHG response on the pico-second and shorter time scale, and today's state of technology implies an all-optical configuration rather than directly applying the voltage from electrodes. Strong electric fields can be generated when the charges get optically generated and then separated, and it is these fields that can drive SHG response. The speed is then limited only by the rates at which the charges recombine and that rate is on a nanosecond scale for the case when the charges (electrons and holes) are created by the

interband absorption in the semiconductor or dielectric. To achieve the shorter decay times one should then consider intraband processes in which the electrons get optically excited to the conduction band, leaving the positively charged holes below the Fermi level. The relaxation of these hot carriers occurs on a sub-picosecond scale enabling various ultrafast applications. Unfortunately, bulk metals are not very efficient absorbers of optical energy as most of it gets reflected, but the situation changes dramatically in small nanoparticles¹⁸⁻²⁰ in the vicinity of localized surface plasmon resonance (LSPR) when the hot carrier generation efficiency can be enhanced by orders of magnitude²¹⁻²⁶. Not only the absorption is enhanced due to field concentration near nanoparticles, but a new channel of the plasmon decay associated with Landau damping^{27, 28, 29} opens up. Landau damping is the process in which the SPP absorption takes place near the nanoparticle surface where the momentum conservation rules are relaxed, hence the hot carriers generated have a higher probability of escaping the metal across a potential barrier which greatly benefits such applications as photodetection³⁰ and surface photochemistry³¹.

In this work we demonstrate that injection of plasmonically generated hot carriers can induce and modulate the SHG in centrosymmetric materials, such as bilayer WSe₂. A bilayer TMDs (*e.g.*, WSe₂) is an appropriate material for investigating the plasmonic hot carriers induced SHG as it was previously shown that the charge-induced SHG originated from an asymmetric screening sheet charge induced by a back-gate potential¹⁰. TMDs have very weak EFISH effect in the uniform field¹⁰. In addition, TMDs with odd number of layers have large intrinsic nonlinearity and the modulation effect from charge injection will be limited. The plasmonic hot electrons transferred to bilayer WSe₂ from the metal can break the inversion symmetry and thus make the SHG appreciable. We demonstrate conclusively the charge injection origin of the SHG by showing that the SHG signal gets quenched when the barrier insulating layer of a hexagonal boron nitride (hBN) is introduced to block the charge transfer.

Our “pump-probe” measurement of the SHG serves as an additional proof that it is the plasmonic hot electrons rather than the strong LSPR electromagnetic field enhanced causes strong SHG. Finally, our transient absorption measurement not only confirms the charge transfer between metal and bilayer WSe₂, but also finds that it occurs on an ultrafast scale of less than 2.0 ps.

Results

Figure 1a displays the schematic diagram of our experiment. The sample consists of bilayer WSe₂ exfoliated from commercial bulk crystal (HQ graphene) onto SiO₂(80 nm)/Si substrate and naturally it is in 2H-stacking order with the centrosymmetry. The layers of the exfoliated WSe₂ can be roughly judged from the optical contrast under optical microscopy and further accurately determined by low frequency Raman measurement of the interlayer vibrational shear and breathing modes as shown in Fig. S1a (Supporting Information). The measured Raman modes at 16.1 and 27.6 cm⁻¹ are the interlayer shear and breathing mode respectively, which are the fingerprints of bilayer WSe₂³²⁻³⁴. Plasmonic nanostructure pattern was created on top of WSe₂ by electron beam lithography (EBL), followed by a thermal evaporation deposition of 30 nm gold directly without any adhesion layer and then followed by a lift-off process. Fig. 1b shows a typical optical image of the WSe₂-metallic nanostructure coupled device. The low frequency Raman measurement also confirmed that the bilayer WSe₂ structure did not change after EBL process. (Fig. S1b). The yellow area (area 1) is the metallic nanostructure and the dark area (area 3) is the bilayer WSe₂, area 2 is the overlapping of metallic nanostructure and bilayer WSe₂ with the nanostructure on top. Fig 1c displays the SEM image of the fabricated gold nanorod (AuNR) on top of bilayer WSe₂ with the length of 200 nm and the width of 50 nm respectively. Fig. 1d shows the reflectivity spectrum of the nanorod array and the resonance wavelength is found to be ~ 900 nm.

SHG measurement was conducted on a spectrometer (Horiba JY HR800) by introducing a Ti:Sapphire femtosecond (fs) pulse laser as excitation source (see methods). For the measurement of sample shown in Fig. 1b, the excitation beam was polarized parallel to NR long axis and the wavelength was 900 nm, in order to excite the dipolar plasmon along the NR long axis. Black curve in Fig. 1e indicates that the SHG signal of bare bilayer WSe₂ (area 3 in Fig. 1b) is not appreciable due to the presence of inversion symmetry⁹. If we zoom in the black curve, a very weak SHG signal can be observed and this is from the substrate-induced interface SHG. For the bare AuNR (area 1 in Fig. 1b), we could observe SHG signal from the AuNR itself, which was attributed to the plasmon enhanced surface SHG of the metallic nanostructure as previous literature reported^{2, 35, 36}. Since SHG power is proportional to the square of the excitation power, this nonlinear process is strongly and resonantly enhanced by the LSPR of the plasmon longitudinal mode. Note that with orthogonal (transverse to the rods axes) polarization, the SHG signal from AuNR will vanish (Fig. S2). In the bilayer WSe₂-AuNR coupled structure, we obtain much higher SHG signal than AuNR as the red curve in Fig. 1e displays. Because the interface SHG in our case is weak, after deducting the SHG from bare NR, we attribute the excess SHG signal to the SHG from the bilayer WSe₂. Note that in both the AuNR and bilayer WSe₂/AuNR coupled structure, the baseline is not flat and we can observe a large background. We attribute this background to the two photon photoluminescence from NR, which emerges from the plasmon enhanced interband transition^{37, 38}. The integrated SHG intensity of bilayer WSe₂ dependent on excitation laser power was plotted in Fig. 1f in logarithmic scale. The linear fitting results in the slope of 2.22, slightly larger than the expected quadratic dependence of the SHG, a significant fact indicating that in addition to serving as a pump for SHG, laser radiation affects it in some other way. We will come back to this point later.

Figure 1. (a) Schematic of the system we studied, plasmon induced hot electrons transfer can establish a non-static separation electric field at the interface, which can perturb the centrosymmetry and produce SHG. (b) Optical image of nanorod-bilayer WSe₂ structure. Point 1, 2, 3 represents the area of nanorod, nanorod/bilayer WSe₂ and bilayer WSe₂ respectively. (c) SEM image of the nanorod array, scale bar is 1 μm . (d) Reflection spectrum of nanorod array with the resonance at 900 nm. (e) SHG signal of Au NR, Au NR/bilayer WSe₂ and bilayer WSe₂, which corresponds to the area 1, 2 and 3 respectively. (f) Power dependent SHG of bilayer WSe₂ in Au NR/WSe₂ structure in logarithmic scale.

As mentioned before the SHG is absent in bilayer WSe₂ due to the centrosymmetry but that symmetry is partially broken when the gold nanostructure is deposited on one side resulting in weak SHG. We speculate that there are two possible mechanisms responsible for the observation of SHG in bilayer WSe₂ coupled to plasmonic structures. The first mechanism is that local electromagnetic field was enhanced dramatically by plasmon resonance, which can further enhance the very weak SHG due to the metal deposition on the bilayer WSe₂. This enhancement reaches maximum at the resonance wavelength excitation of the surface plasmonic modes. The second mechanism is the hot carrier charge injection from

the AuNR into the bilayer WSe₂, which engenders symmetry-breaking electric field and thus induces the SHG.

In order to distinguish between these two mechanisms, we have performed a second experiment in which an hBN insulating spacer between AuNR and WSe₂ had been added. This hBN barrier was intended to block any possible charge injection from the AuNR, without disturbing the local optical field enhancement. Layered hBN was exfoliated from the bulk crystal and it was transferred on top of WSe₂ with precise alignment under optical microscope. Fig. 2a displays the optical image of hBN-bilayer WSe₂ heterostructure. Subsequently the AuNR was fabricated on the hBN-bilayer WSe₂ heterostructure with the same EBL procedure as described previously. In this sample the length and width of NR is 160 and 50 nm respectively. The resonance is 794 nm (Fig. S3) so that we use the 800 nm fs laser excitation for SHG measurements. SHG was measured on different overlapping configuration on the same sample with the same measurement conditions. As expected, the SHG of bare bilayer WSe₂ was not observed as black curve in Fig 2b shows, and the AuNR SHG arise from the plasmon enhanced SHG (red curve in Fig. 2b). The SHG of NR-bilayer WSe₂ (blue curve in Fig. 2b) is much stronger than bare AuNR because the additional contribution of the bilayer WSe₂, which is consistent with Fig 1e. However, in the configuration AuNR-hBN-bilayer WSe₂ with a 4L hBN spacer, the SHG intensity had been reduced to the same level as bare AuNR (green curve in Fig. 2b), which suggests that the contribution from bilayer WSe₂ had been eliminated. The SHG of AuNR/bilayer WSe₂ in Fig. 2b is stronger than Fig. 1e, which may arise from the different excitation wavelength. Previous literature showed that the SHG of TMDs was higher when the excitation wavelength matches the exciton resonance^{39,40}. In our case, 800 nm excitation in Fig. 2b is closer to the A exciton resonance (770 nm) and may produce higher SHG than the 900 nm excitation as shown in Fig. 1e. In addition, the non-flat baseline in Fig.1e than Fig. 2b is due

to the fact that the SHG wavelength in Fig. 1e (450 nm) is closer to the center peak of the two photon luminescence (~ 600 nm). To determine whether introduction of spacer alters the field significantly, we have calculated E-field distribution on the top surface of WSe₂ without and with hBN spacer at the resonance wavelength as shown in Fig. 2c, 2d respectively, with the “hot spot” at the four corners being telltale signs of LSP resonance. The relevant SHG enhancement of the square of optical power $|E|^4$ for two configurations was found to be 1.25×10^5 and 2.35×10^5 , respectively. The local E-field on the top WSe₂ surface with hBN spacer is slightly higher than without hBN spacer, however, the SHG signal with hBN is much weaker than that without hBN, which suggests that the E-field enhanced SHG can be excluded and the charge injection is indeed the main enhancement mechanism. The mechanism had been explained in our prior work¹⁰. The injected hot electrons are spatially separated from the holes remaining at the surface of metal rods thus engendering a very strong electric field that breaks the inversion symmetry and enables SHG.

Figure 2. (a) Optical image of bilayer WSe₂/hBN. (b) SHG signal of NR, bilayer WSe₂, NR/bilayer WSe₂ and NR/hBN/bilayer WSe₂. (c) and (d) are simulated E-field distribution at the top surface of WSe₂ without and with hBN as a spacer. The E-field are almost same with and without hBN layer, which indicates that the SHG is not from the E-field enhancement.

To further validate the mechanism of plasmonic hot electron induced SHG, we have performed “pump-probe” measurements as displayed in Fig. 3a. We use an 800 nm fs laser as the SHG probe light and the SHG signal is collected at 400 nm. Here the 800 nm fs laser is far away from the plasmonic resonance, so that the fs laser cannot generate large numbers of hot carriers. A continuous wavelength (CW) laser is employed as the pump light to induce the plasmonic hot carrier injection. The rate of plasmon-induced hot electron injection depends on the CW pump laser wavelength and power. Hot carrier injection can only be efficient when the laser wavelength overlaps with the plasmon resonance wavelength. Also, quite naturally, CW laser with higher power can generate more plasmonic hot electrons. For the “pump-probe” measurement we have chosen a nanodisk array instead of the nanorod, to eliminate the polarization anisotropy. Two kinds of nanodisks with a diameter of 70 and 150 nm were fabricated on top of bilayer WSe₂ and their plasmon resonance wavelengths were 538 and 722 nm (Fig. 3b). We chose 532 nm CW laser (red vertical line in Fig. 3b) which can only excite the plasmon resonance of 70 nm disk but not the 150 nm disk. The spots of CW laser and fs laser were aligned on the same point on the disk-bilayer WSe₂ sample and the power of the fs laser was fixed during SHG measurement.

As shown in Fig. 3c, for the 70 nm array, the increasing 532 nm CW laser can induce higher SHG intensity. While for the disk with a diameter of 150 nm shown in Fig 3d, the nanodisk array is off resonance under 532 nm illumination, the SHG signal is almost unchanged with the increasing power of 532 CW laser. These results indicate that only in the case when the pump laser (532 nm) can excite the plasmon resonance, the increased laser power can generate more hot electrons and thus increase the SHG intensity, which confirms our hypothesis that plasmonic hot electrons induce the SHG of bilayer WSe₂. One can observe some SHG signal when the 532 pump laser is off on all those 70 and 150 nm samples. It is most probable that this rather weak SHG originate from the interface SHG in the

disk/bilayer WSe₂/SiO₂ configuration. Because the 800 nm fs fundamental laser cannot excite the plasmon resonance of disk, the SHG of Au disk was negligible (see Fig. S4) and the SHG observed was mostly from bilayer WSe₂. The related effective $\chi^{(2)}$ normalized to the value when the 532 nm laser is off is plotted in Fig. 3e. It can be seen that only in 70 nm diameter disk, the effective $\chi^{(2)}$ can be enhanced as large as 3 times with increasing pump laser power while in the 150 nm disk sample $\chi^{(2)}$ is almost unchanged. For the 70 nm disk in Fig. 3c, the SHG saturates with further increasing pump laser power, which is consistent with previous literature on TMDs monolayer MoS₂⁴¹. On the other hand, we fix the disk with one certain diameter (70 nm) and then vary pump laser wavelength to control the plasmonic hot electrons injection. The normalized second-order susceptibility is plotted in Fig. 3f. Similar results can be observed, *i.e.*, only when the pump laser is in resonance with the disk, the increasing laser power can induce higher SHG signal from bilayer WSe₂ sample (the reflection and SHG intensity details are shown in Fig. S5). Relying on the fact that increasing laser power can induce more plasmonic hot electrons, we can explain why the slope in Fig. 1f is larger than 2. In this case, SHG intensity $I_{shg} \sim aI^2 f(I)$ here $f(I)$ indicates the factor from hot electrons which is proportional to separation field E_{sep} , consequently the slope is larger than 2 (a and I in the equation refer to a constant and the excitation laser intensity, respectively). In addition, polarization dependent SHG was measured and six fold symmetry was observed, which indicates that the SHG is indeed from the bilayer WSe₂ (see Fig. S6).

Figure 3. (a) Schematic of pump-probe measurement with a CW laser to manipulate the SHG signal. (b) Reflection of two samples with the disk diameter of 70 and 150 nm, the red vertical line indicates the 532 nm CW pump laser. (c) and (d) are the SHG intensity of bilayer WSe₂ with increasing 532 nm CW laser power for the sample with disk diameter of 70 and 150 nm respectively. (e) Second-order susceptibility of bilayer WSe₂ at various pump laser power normalized to the value without pump laser for 70 nm and 150 nm disk respectively. (f) Second-order susceptibility of bilayer WSe₂ for a fixed nanodisk (70 nm) at 514, 532 and 785 nm CW pump laser respectively. (the reflection and SHG intensity plot are shown in Fig. S5 in supporting information.)

Transient absorption measurement is a powerful technique which we used not only to further verify the presence of injected carriers in WSe₂ but also to elucidate the dynamics of this hot carrier injection. For this purpose, the sample had to be fabricated on transparent sapphire substrate as shown in Fig. S7. The sample size is around 50 μ m and it is compatible with the probe beam size in the transient absorption measurement. The A exciton absorption of bilayer WSe₂ is around 750 nm and the plasmon resonance of disk is around 825 nm (see

Fig. S7). As Fig. 4a shows, for the bare bilayer WSe₂, no exciton dynamics is observable with 850 nm pump laser having photon energy much lower than the A exciton absorption band (750 nm). However, for the disk/bilayer WSe₂ system (Fig. 4b), we can clearly observe the A exciton bleaching under the same 850 nm pump excitation. The 850 nm pump laser radiation, while it cannot excite carriers in WSe₂ directly, is capable of exciting hot carriers in the metal disk that are then injected into bilayer WSe₂^{42, 43} and occupy the conduction band of WSe₂ (process shown in Figure 4d), consequently reduce the probability of electron transition from valence band to conduction band and lead to the bleaching effect⁴⁴. The process at 700 nm is the electron-phonon relaxation of the Au disk⁴⁵. Currently we are not able to classify the broad process at 500-600 nm as it was also observed in the Au nanorod in the literature⁴⁶. By bi-exponentially fitting this A exciton kinetics we can obtain the rise time of 119.0 fs and the decay lifetime of ~1.84 ps (Fig. 4c), which correspond to the plasmonic hot electrons generation and transfer time (consistent with 100- 200 fs reported in literature⁴⁷) and the electron-hole recombination time respectively. The electron-hole recombination occurs at the metal surface once the hole makes its way there and it is this time that ultimately determines the speed with which SHG power can be modulated.

Figure 4. (a) Transient absorption of bare bilayer WSe₂ under 850 nm pump excitation and no bleaching of A exciton was observed. (b) Transient absorption of bilayer WSe₂/ Au disk coupled structure and bleaching of A exciton was observed under 850 nm pump excitation. (c) Decay kinetics of the A exciton with bi-exponential fitting. (d) Schematic of plasmonic hot electrons transfer.

Conclusion

A metallic nanostructure/bilayer WSe₂ coupled system was designed to investigate the plasmonic hot carriers manipulated SHG. The decay of localized surface plasmons of Au nanorods results in generation of electron hole pairs with energetic hot electrons injected into the bilayer WSe₂ leaving the less energetic holes behind. The separation electric field stemming from this charge transfer was responsible for the induced SHG. Previously it has been reported that the SHG can be actively controlled by bias voltage^{10, 48}, here we demonstrated efficient and agile SHG control *via* injection of the plasmonic hot carriers on an ultrafast time scale. Our working hypothesis of hot carrier injection being responsible for

SHG has been further substantiated by comparing the configuration with and without h-BN in between metal nanostructure and bilayer WSe₂. These experiments unequivocally confirmed that the induced SHG was indeed due to charge injection but not the E-field enhanced effect. Further analogous “pump-probe” study indicates that only when the pump laser is in resonance with the nanostructure plasmon, the hot electrons injection gets enhanced and thus induce higher SHG. This resonant behavior verified that the plasmon induced hot electrons injection was responsible for the SHG in bilayer WSe₂ instead of the direct photon excited electrons. This is expected as the electric field of plasmons is concentrated near the surface and that is where the hot electrons are generated so they can rather easily be injected into the WSe₂. The presence of injected carriers has been verified by transient absorption study which has also allowed us to determine the rise and fall times of 119 fs and 1.84 ps, respectively. This fast response creates opportunity for efficient ultrafast control of SHG, something that is unattainable with the conventional EFISH. With the pump-probe configuration one can think of “*three terminal all-optical device*” in which the pump intensity modulates or switches the SHG output enabling logical operations on the ultra-fast scale.

Methods

Sample preparation. Bilayer WSe₂ was exfoliated on to SiO₂(80 nm)/Si substrate. A PMMA A4 (Microchem, USA) resist was spin-coated on the sample and then baked at 180°C for 18 mins. We then used a scanning electron microscope (JEOL 7001F) equipped with the nanometer pattern generation system (NPGS) to pattern nanostructures on bilayer WSe₂ directly. The exposed chip was immersed in MIBK:IPA (3:1) mixed solution for 90 seconds to finalize developing. After developing, the sample was loaded into a thermal evaporator (Elite Engineering, Singapore) to deposit an Au film with a thickness of 30 nm without any adhesion layer. Subsequently, the chip was immersed in acetone for lift-off procedure. The sample was ready after rinsing with IPA and then drying with nitrogen gas. For the sample on sapphire for the TA measurement, the sample preparation was followed similarly and the only difference was that a thin ITO layer was sputtered on sapphire to avoid the charging effect during electron beam lithography process.

Optical measurement. 1) For the reflection, transmission and absorption measurement, we used a microspectrophotometer (Craic 20) to measure the small size sample and it is capable to measure the sample size down to 10 μm . The measurement range can be covered from 400 to 2100 nm. 2) Low frequency Raman measurement was carried out on a micro-Raman spectrometer (Horiba-JY T64000) equipped with a liquid nitrogen charge-cooled device. The first two gratings were configured as subtractive mode which enables the measurement down to 5 cm^{-1} Raman shift. We used a 532 nm (0.17 mW) solid laser as the excitation, which was filtered by a Bragg grating to remove laser sidebands and then by a ruled reflecting grating (specify the line/mm). Backscattering signal was collected by 100X objective and then dispersed by a 1800g/mm grating before entering into the CCD. 3) SHG measurement was conducted on Raman spectrometer (Horiba-JY HR800) by introducing a femtosecond laser. Femtosecond laser with 100 fs pulse width and 80 MHz repetition rate was produced from

MaiTai Ti:Sapphire oscillator (Spectra Physics) with the wavelength range of 690-1040 nm. A visible-near infrared beam splitter was utilized to direct the laser beam onto the 100X objective and shine on the sample. Before the backscattered light entering CCD, a 520 nm short-pass filter was added to eliminate the laser beam and let the SHG signal pass through. 4) Transient absorption measurement was conducted on femtosecond transient absorption spectrometer (HELIOS, Ultrafast Systems), pump beam was generated from the TOPAS Prime optical parametric amplifier with 800 nm input femtosecond laser. The wavelength of generated pump beam can be adjusted from UV to infrared (189-2000 nm) and the beam diameter is around 100 μm . Probe beam is generated with CaF_2 crystal with the wavelength range from 400-800 nm, and the beam diameter is around 50 μm .

Additional information

Supporting information is available

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Author contributions

X.L.W and Q.H.X conceived the idea and designed the research; X.L.W. fabricated all the samples, X.L.W, W.G.X., and W.J.Z performed the optical measurement. X.L.W, W.G.X,

W.J.Z, J.B.K and Q.H.X analyzed the data; X.L.W, J.B.K. and Q.H.X wrote the manuscript.

All authors discussed and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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