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Localized Emission from Laser-Irradiated Defects in Two-Dimensional Hexagonal Boron Nitride

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Abstract: Hexagonal boron nitride (hBN) has emerged as a promising two-dimensional (2D) material for photonics device due to its large bandgap and flexibility in nanophotonic circuits. Here, we report bright and localized luminescent centres can be engineered in hBN monolayers and flakes using laser irradiation. The transition from hBN to cBN emerges in laser irradiated hBN large monolayers while is absent in processed hBN flakes. Remarkably, the colour centres in hBN flakes exhibit room temperature cleaner single photon emissions with $g^2(0)$ ranging from 0.20 to 0.42, a narrower line width of 1.4 nm and higher brightness compared with monolayers. Our results pave the way to the engineering the deterministic defects in hBN formed by laser pulse and show great prospect for application of defects in hBN used as nano-size light source in photonics.

Keywords: two-dimensional materials, hexagonal boron nitride, single photon source, atomic defects, laser irradiation, colour centres
INTRODUCTION

Unique optical properties of two-dimensional (2D) semiconductors such as graphene, transition metal dichalcogenides (TMDCs), and boron nitride have attracted considerable attention[1-7]. Among all potential electronics device, photoelectrical properties of 2D hexagonal boron nitride (hBN) are of great important due to its wide bandgap[2, 8-10], graphene-like structure[5, 11-14], high thermal conductivity[15, 16] and chemical stability[17, 18]. From this perspective, fluorescent properties of hBN monolayers have been explored since ultra violet emission in hBN monolayers was reported[6, 19-23]. Particularly, engineering the luminescent centres in hBN is an aspiring goal because the centres are excellent room temperature single photon emitters[24, 25]. To this extent, localized and patterned defects are strongly preferred to form sub bandgap excitation sources in hBN monolayers while preventing excitonic combination[8]. Defects engineering in hBN can be achieved mainly by annealing[24, 25], electron[24, 25] or ion beam[26] irradiation, and wrinkle process[27]. The defects origins could be predicted as three stable native point defects in hBN monolayers defined as a boron vacancy (VB), a nitride vacancy(VN) and N_B V_N in which one nitrogen atom is missing and the boron site is occupied by nitrogen[28, 29]. Toan Trong Tran et. al. created atomic point defects in hBN monolayers using annealing and electron beam, finding that the photoluminescence (PL) peak around 623 nm was closely related with N_B V_N point defect and attributed to the zero phonon line (ZPL) with single photon characteristics[24, 25]. However, the colour centres created by annealing, electron beam and wrinkling in hBN monolayers are uncontrollable and distributed randomly.

Although the electron beam irradiation with high voltage generates smaller beam focus than that of laser irradiation, laser irradiation can be conducted at ambient environment with no vacuum requirement, which is more simple and flexible. Laser irradiation is now widely used owing to its flexibility to control the energy and position. Laser irradiation was previously utilized to fabricate nanostructures[30-33], graphene
oxide deposition[34, 35] and synthesis of nanowires[36-38]. Laser irradiation is also used to create colour centres in cBN crystal[39] and diamond[40], although the emission is very weak with broad peaks. As it can be seen, it is easier to find colour centres employing laser irradiation. Here, with laser irradiation technology, we successfully engineered colour centres in hBN monolayers and hBN flakes. Interestingly, hBN-to-cBN transition emerges around the laser irradiation region in hBN monolayers, which was not reported from voids created by laser irradiation in single crystal of cubic boron nitride (cBN)[39]. The strong and sharp emission of addressed colour centres is mainly found surrounding voids. Fine emissions with a full width at half-maximum (FWHM) of 4.5 nm and 1.4 nm are found in laser irradiated hBN monolayers domains and flakes, respectively, of which both are much narrower than that of ~10 nm from defect emission created by electron beam irradiation[25]. Colour centres in hBN flakes are much brighter than that in hBN monolayers and poor single photon emitters are found in irradiated hBN monolayers while bright narrowband single photon emissions with $g^2(0)$ as low as 0.20 are detected in hBN flakes. Additionally, there is hitherto no report on the quantum properties from localized defects in hBN monolayers and flakes created by laser irradiation. Our results not only reveal optical properties of colour centres in laser irradiated hBN, but also provide a new approach to engineering controllable defects in hBN.

**MATERIALS AND METHODS**

**Sample fabrication.** 2D hBN monolayers were obtained using CVD method as reported previously[41]. With the ammonia borane (Sigma-Aldrich) heated at 85 °C and the amount controlled at around 10 mg, the hBN monolayers were grown on copper at a fixed temperature of 1050 °C for 0.5 h after annealing the copper. The growth was done under Ar (200 sccm) protection with a small amount of H₂ (18 sccm). After growth, the hBN was transferred onto SiO₂/Si substrate using electrochemical delamination[42]. Finally, the sample was annealed in tube furnace at 850 °C for 0.5 h with argon flow and then cooled to room
temperature. hBN flakes were prepared by directly drop casting 50 μL commercial BN pristine flakes solution (Graphene Supermarket) onto SiO2/Si substrate and dried at room temperature.

**Laser irradiation setup.** Laser pulse (Chameleon Ultra Laser System) of τ\textsubscript{p} = 140 ± 20 fs duration was focused on the surface of hBN monolayers with a lens of numerical aperture NA= 0.65 (Olympus 40×). The laser irradiation was performed at fundamental λ=700 nm with repetition rate of 80 MHz for 1 s in Figure 1 ~ 3 and 0.5 s for Figure 4, Figure 5 and Figure 6.

**Surface characterization.** LEO 1550 Gemini was used to take scanning electron microscope (SEM) images. Atomic force microscope (AFM) setup equipped with Cypher scanning probe microscope and Asylum Research MFP-3D was used with tapping mode to characterize the morphology of samples.

**Raman measurement.** Raman spectra was conducted using 532 nm 37 μW continuous wave laser (WITec focus innovations) with microscope objective numerical aperture NA=0.8 (Olympus 100x). The Raman was operated at the diffraction limit with a laser spot size of less than 1 μm. The PL mapping was performed using Raman set up with the same excitation laser and objective. The scanning step of Raman and PL intensity mapping is 0.2 ~ 1 μm/step.

**Photon antibunching measurements and data fitting.** Photon antibunching was performed using the HBT (Hanbury Brown and Twiss) setup with continuous wave laser at 532 nm at 40 μW and two photon counting detector modules (PDM) from Micro Photon Devices connected to single-photon counting acquisition module (PicoHarp 300). We filtered emission with linear variable filters (Ocean Optics LVF-HL) and fluorescence bandpass filter at 630 ± 38 nm from Semrock (FF01-630/38-25). The results in Figure 4d were fitted with the following standard expressions[43]:

\[
g^2(\tau) = 1 - (1 - g^2(0)) e^{-|\tau|/\tau_{\text{tot}}}\tag{1}
\]

where \(\tau_{\text{tot}}\) is interlevel rate constant related to the lifetime of combination and pumping, and defined as:
\[
\frac{1}{\tau_{\text{tot}}} = \frac{1}{\tau_{\text{rec}}} + \frac{1}{\tau_{\text{pump}}}
\]

where \(\tau_{\text{rec}}\) and \(\tau_{\text{pump}}\) are the lifetimes of photon recombination and pumping, respectively. In this paper, we use low power laser excitation (40 \(\mu\)W), thus \(\tau_{\text{pump}}\) can be considered as infinite compared with \(\tau_{\text{rec}}\) and then:

\[
\tau_{\text{tot}} \approx \tau_{\text{rec}}
\]

The defect can be confirmed to be single photon emitter once \(g^2(0) \leq 0.5\)\(^{[44]}\). The long time scale second order autocorrelation data was fitted using three-level model\(^{[45]}\):

\[
g^2(\tau) = a + b e^{-\tau/\tau_2} + c e^{-\tau/\tau_3}
\]

where \(a\), \(b\) and \(c\) are constants while \(\tau_2\) and \(\tau_3\) are related to the interlevel rate constants.

**PL measurements.** Microphotoluminescence measurements were performed using free space excitation and collection through visible–near infrared microscope objective (Olympus 80\(\times\), NA = 0.90)\(^{[46]}\). The samples were excited with a ps-pulsed laser diode emitting at 371 ± 5 nm wavelength with 10 MHz repetition rate, focused to a beam size of 2 \(\mu\)m. Luminescence was detected using a Peltier-cooled photomultiplier tube (Hamamatsu H7422 series) coupled to a grating spectrometer (Edinburgh Instruments F900 and Bentham TMS300). Time-resolved decay traces were acquired by a time-correlated single-photon counting acquisition module (Edinburgh Instruments, TCC900) at selected wavelength of 626 ± 5 nm. The PL images were recorded using charge coupled device (CCD) camera with a band pass filter of 625 ± 20 nm.

**RESULTS AND DISCUSSION**
The hBN monolayers were synthesized using chemical vaper deposition (CVD) method and then transferred to SiO$_2$/Si substrate, see Methods. Before hBN monolayers were irradiated, the as-grown hBN monolayers were characterized with Raman and atomic force microscope (AFM). The Raman exhibits a peak of 1370 cm$^{-1}$ and the thickness of monolayers from AFM characterization is ~ 2.8 nm, see Supplementary Information Figure S1. Both features are the signatures for pristine hBN monolayers. Then, we created defects in these monolayers by laser irradiation under ambient environment, see Methods.

Before we characterized emission properties of the defects, we needed to confirm the presence of hBN monolayers around the void. When applying high energy to hBN, there could be a chance for phase transition$^{[47, 48]}$. To verify this, Raman measurement was carried out around the irradiated void. Figure 1a shows the Raman spectra of points along the line in Figure 1c which is passing through the void with a diameter around 1.5 μm. The Raman peaks around 1,460 and 1,370 cm$^{-1}$ indicating the substrate of silicon and hBN respectively$^{[49, 50]}$. The centre of void shows no peak of 1,370 cm$^{-1}$ as no hBN monolayers are left after the laser irradiation. The Raman spectrum of crystal cBN can be characterized with two isolated transverses optical (TO) mode at 1056 cm$^{-1}$ and longitudinal optical (LO) vibrational mode at 1305 cm$^{-1}$$^{[51]}$. However, the changes of TO and LO occur as a function of cBN crystal size$^{[52]}$. In nano-crystal cBN, TO mode disappeared while the LO mode was short shifted and got broadened. These previous results are well related with the data here, indicating the obvious peak of 1295 cm$^{-1}$ at L2 and L5 in Figure 1a is due to the presence of nano-crystal cBN. The small G band around 1600 cm$^{-1}$ at L2 and L5 comes from the carbon contamination which may be induced from hydrocarbon during laser processing or the residual of polymethyl-methacrylate (PMMA) during transfer. Due to low intensity of G band, the content of carbon is extremely low that can be ignored in the following discussion. On the other hand, the Raman spectra of points along the curve is almost the same in Figure 1b, indicating the phase
components in transition region are homogeneous hBN to cBN transition. This structural transformation is attributed to the high energy of laser irradiation and the spectra is similar to that of transformation from hBN to cBN due to the applied He$^+$ ion implantation[26].

![Figure 1. Raman spectra of hBN monolayers.](image)

(a-b) Raman spectra corresponding to the points on line (a) and curve (b) marked in (c). (c) The microscope of void in hBN with points L1, L2, L3, …L7 on the line and points C1, C2, C3 on the curve. The arrows show the order of these points and L2, L5 are the intersectional points of curve and line. Excitation wavelength of Raman is 532 nm. The scale bar of microscope image is 5 μm. The void is created by laser at 1.93 W.

hBN to cBN due to the applied He$^+$ ion implantation[26].
Transient PL spectra of the laser irradiation region was recorded over a large area using confocal microscopy with a $371 \pm 5$ nm laser excitation. The main narrow PL peak at 624 nm is fitted with Gauss in Figure 2a, and this wavelength with FWHM of 10.6 nm matches very well with 623 nm emission from $\text{NB}_{\text{V}}\text{N}$ point defects[24] whereas the broad sub peak around 640 nm is similar with the PL emission from cBN colour centres[53].

The optical radiative transition lifetime was carried out using time resolved fluorescence measurements over a large scale up to 500 ns (Figure 2b). The signals were fitted by a single exponential function with 4 ns and 166 ns for short decay and long decay, respectively.

To further study the type of emission centre, emission polarization test was conducted as shown in Figure 2c to gain further insights into the relationship between polarization of excitation and emission. Fitted by $\cos^2(\theta)$ function, the results indicate that the emission at 624 nm is linearly polarized with dipole characteristics[54] and the polarization is coinciding with that of excitation. Thus, the polarization of emission can be easily controlled by excitation.

**Figure 2. Emission properties of laser irradiation region in hBN monolayers.** (a) Room temperature PL spectra of laser irradiated region with Gauss multi peaks fitting. (b) Time resolved photoluminescence decay curve fitted with exponential function (white). (c) Emission polarization curve (black balls) with $\cos^2(\theta)$ function fitting (red solid line). The excitation in (c) is vertically polarized (blue solid line). All measurements were conducted using a $371 \pm 5$ nm, 50 mW laser and at room temperature.
Figure 3a and b exhibit the PL intensity mapping at 624 nm at different regions marked in Figure 3c and the mapping was conducted with a step of 1 μm. One circular area in the centre with much lower PL intensity in contrast to the transition region can be clearly observed in Figure 3b. And the pristine region is also as dark as central circular area (Figure 3a, b), which means there are much less colour centres at pristine regions compared with transition region. The highest PL intensity is up to 1,930 counts/s at transition region which consists of hBN and cBN according to Raman spectra Figure 1. The PL mappings further prove that the enhanced sharp emission in PL spectra in Figure 2a comes from the colour centres in hBN and cBN transition region. These results illustrate that the bright colour centres are created by laser irradiation not by thermal annealing.

To gain further insights to the characters of defects, single atomic defect is preferred for the characterization and it is easier to get separate single atomic defect at small monolayers domains, see Supplementary Information Figure S2. To this extent, we performed PL intensity mapping measurement with high resolution of 0.2 μm/step at another irradiated region. Unlike the region in Figure 3, the hBN monolayers in this experiment comprise of small monolayers domains and its presence can be identified.

**Figure 3. PL mappings around laser irradiation region for monolayers.** (a-b) PL intensity mapping of blue square (a) and red square (b) in microscope (c); (c) Corresponding optical microscope image of laser irradiated hBN monolayers. The scale bar in the micrographs is 10 μm. The void is created by laser at 1.93 W.
by Raman mapping in Supplementary Information Figure S3. Figure 4b shows bright luminescent spot with 2,100 counts/s in scanning confocal PL mapping of hBN monolayers around the irradiated region as marked in Figure 4a and this may correspond to the emission from single defects. The diameter of the void is \( \sim 1 \mu m \), see Supplementary Information Figure S2. We also observed the Raman peak at the same spot of hBN monolayers in the Raman mapping, see Supplementary Information Figure S3. The area of PL and Raman peak spot is about \( 0.5 \times 0.5 \mu m^2 \), which is more or less the same size as the diffraction limit of the confocal setup. This area reflects the nanometre size of monolayers domains, also see Supplementary Information Figure S2. Unlike Figure 2, we performed experiments in another defects with longer excitation wavelength of 532 nm and we expect the emission properties in Figure 4 may differ from those in Figure 2[25, 55]. To verify this assumption, PL spectra and autocorrelation functions over long time scales were conducted, which can offer information on metastable states with long time decay[56, 57]. Figure 4c taken from the bright spot in Figure 4b shows the narrow emission at 628 nm with FHWM of 4.1 nm, which is much better than that of 10.6 nm in Figure 2 and the previous electron-beam irradiated
hBN monolayers[25]. The slight shift of emission wavelenght between Figure 2a and Figure 4c is related with the diversity between different setups, which is still in the accuracy of the setup. The sub-peak of 640 nm in Figure 2a disappeared in Figure 4c in the small monolayers domain with the absence of cBN in the Raman mapping at the same region, see Supplementary Information Figure S3. To identify single photon sources, Hanbury - Brown - Twiss (HBT) interferometry antibunching experiments were carried out to record second order autocorrelation functions. Figure 4d illustrates $g^2(\tau)$ curve for the emission of 628 nm at room temperature, indicating photons antibunching with $g^2(0) \sim 0.50$ with poor single photon emitter and a lifetime $\tau_{\text{tot}}$ of 3.7 ns, consistent with the lifetime value measured by time resolved photoluminescence decay at irradiated large monolayers. Longer time scale second order autocorrelation

![Image of optical micrographs and PL spectra](image-url)
function is shown in Figure 4e. Fitted with multiexponential (see methods) function, we obtained additional decay times: $\tau_2 = 374 \text{ ns}$ and $\tau_3 = 1.7 \mu\text{s}$.

Compared with large monolayers, the hBN monolayers domains intend to show narrower emissions after laser irradiation. Thus, we arise an assumption that the optical properties are closely related to size of hBN and hBN flakes with smaller size of \~200 nm should exhibit better optical properties. To verify this, we performed laser irradiation onto hBN monolayers and flakes with different laser powers. Figure 5 shows optical properties of hBN monolayers and flakes after femtosecond laser processing. Bright fluorescence was clearly observed at irradiated regions, indicating the formation of optically active defects or colour centres. The defects in hBN monolayers have almost the same wavelength of emission with that in flakes,
suggesting the same type of defects are induced by laser (Figure 5a and f). More importantly, we found narrow emissions (1.4 nm width) in hBN flakes without damaging substrate after low laser power processing. However, fluorescence was no longer observed from hBN monolayers after laser processing without damaging substrate, suggesting the absence defects. This is due to hBN monolayers have a wide bandgap (~6 eV) and the thickness (2.8 nm) is too low to absorb the energy of laser, resulting in most energy of laser is transferred into substrate and no defect is created. At the same excitation, hBN flakes have much stronger fluorescence than monolayers (Figure 5a, b, d, e and f), indicating that it is easier to create colour centres in hBN flakes than monolayer.

**Figure 5. Generation of localized colour centres in hBN monolayers.** (a-c) and flakes(d-g). (a,b) PL intensity mapping of laser irradiated regions in hBN monolayers. Inset: a typical PL spectrum taken from the blue circle in (a). (c) Corresponding microscope image of (a,b), and the implemented laser powers are: 1.25 W, 0.89 W, 0.53 W, 0.27 W and 0.10 W from right to left. (d,e,f) PL intensity mapping of laser irradiated regions in hBN flakes. Inset: a typical PL spectrum taken from the bright spot in (f). (g) Corresponding microscope image of (d,e,f), and the implemented laser powers are: 1.60 W, 1.25 W, 0.89 W, 0.53 W, 0.27 W and 0.10 W from left to right. Scale bar: 10 μm.
From Figure 5d, e and f, plenty of separate bright colourful spots were created after laser processing, of which the majority are attributed to single defects hosted by hBN flakes. Figure 6 presents the lowest and highest $g^2(0)$ among all measured single photon emitters in hBN flakes with corresponding PL images. Each spot is measured at room temperature using a 40 $\mu$W excitation laser with an acquisition time of 20 s and were normalized (without background correction). The fitting reveals the values of $g^2(0)$ ranges from 0.20 to 0.42 among all single photon emitters in hBN flakes in Figure 5g. The fitted values of $\tau_{rot}$ in Figure 6a and b are 3.4 ns and 3.2 ns, respectively. Figure 6c and d show the diameter of bright spot is $\sim$ 650 nm which is the diffraction limitation of CCD camera, indicating true diffraction limited optical centre is successfully induced. The bright spot in Figure 5f also demonstrates single photon emission with $g^2(0) = 0.25$, indicating one single photon emitter can be deterministically engineered by laser processing without damaging substrate.

Figure 6. Single photon emitters in hBN flakes. (a,b) Second order autocorrelation functions curves from individual colour centres in hBN flakes (red and blue open circles). Solid red and blue lines are fits using equation. (c,d) PL images corresponding to (a) and (b). Scale bar: 1 $\mu$m.
CONCLUSION

In conclusion, we successfully created colour centres in hBN monolayers and flakes via laser irradiation and find the transformation from hBN to cBN at large hBN monolayers region. The strong and sharp emission matches well with that of NbVN like point defects in hBN. Laser processed hBN flakes intends to exhibit sharper emission, brighter colour centres and better single photon emissions compared with monolayers. Our results offer a new approach to engineering defects in hBN and motivate more endeavours to explore further the optical properties of 2D materials in the application of photonics and quantum technology using laser irradiation.

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