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Ultra-bright emission from hexagonal boron nitride defects as a new platform for bio-imaging and bio-labelling

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ABSTRACT

Bio-imaging requires robust ultra-bright probes without causing any toxicity to the cellular environment, maintain their stability and are chemically inert. In this work we present hexagonal boron nitride (hBN) nanoflakes which exhibit narrowband ultra-bright single photon emitters[1]. The emitters are optically stable at room temperature and under ambient environment. hBN has also been noted to be noncytotoxic and seen significant advances in functionalization with biomolecules[2,3]. We further demonstrate two methods of engineering this new range of extremely robust multicolour emitters across the visible and near infrared spectral ranges for large scale sensing and biolabeling applications.

Keywords: hexagonal Boron Nitride, 2D materials, multicolour, biolabelling

1. INTRODUCTION

In recent years, fluorescent nanodiamonds, quantum dots and upconversion nanocrystals have been considered as candidates for bio-labelling and intracellular imaging.[1-3] These materials exhibit known luminescence at a particular wavelength or over a narrow spectral range. In this work, we present an unprecedented new system – namely hexagonal boron nitride (hBN) nanoflakes, which contain color centers emitting over a broad range of emission wavelengths and can have enormous potential for bio applications.

hBN is an emerging two dimensional material in the field of nanophotonics due to the recent discovery of room temperature single photon quantum emitters[4] and the following inquest into its unique optical properties[5]. As hBN is a wide bandgap material of ~6eV, it is able to host many optically active defects at room temperature over a broad range spanning the visible and the near infrared spectral ranges.[5] The emitters exhibit narrow line widths of sub 10 nm at room temperature, and a short excited state lifetime, and high brightness.[4]

In this paper we demonstrate two methods of engineering a new range of multicolour room temperature emitters across the visible and near infrared spectral ranges with deterministic and high throughput for large scale sensing and biolabeling applications[2]. Furthermore, we show the created emitters are ultra-bright, extremely robust and optically

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stable with no signs of photobleaching or photoblinking under ambient environment and when exposed to high temperature.[5] hBN has also been noted to be extremely chemically inert, non-toxic, does not interact with the cellular environment and has seen significant advances in functionalization with biomolecules.[6,7] Combined with the emission wavelengths of these emitters which span the range of 550-800nm, make this an ideal candidate for applications, such as quantum yield enhancement, bio-imaging and biosensors.

2. EMITTER FABRICATION

The methods for engineering luminescent defects in hBN include annealing and electron beam irradiation, a schematic of these processes are shown in figure 1a. The solution of hBN nanoflakes was initially dropcast onto a silicon (111) substrate[4] for both cases of engineering methods. The annealing treatments were performed under 1 Torr of Argon for 30 minutes with various annealing temperatures. The normalized rate of stable color centers created is shown in figure 1b. Increase in annealing temperature leads to an increase in the formation of color centers due to defect diffusion and lattice relaxation occurring in hBN.[5]

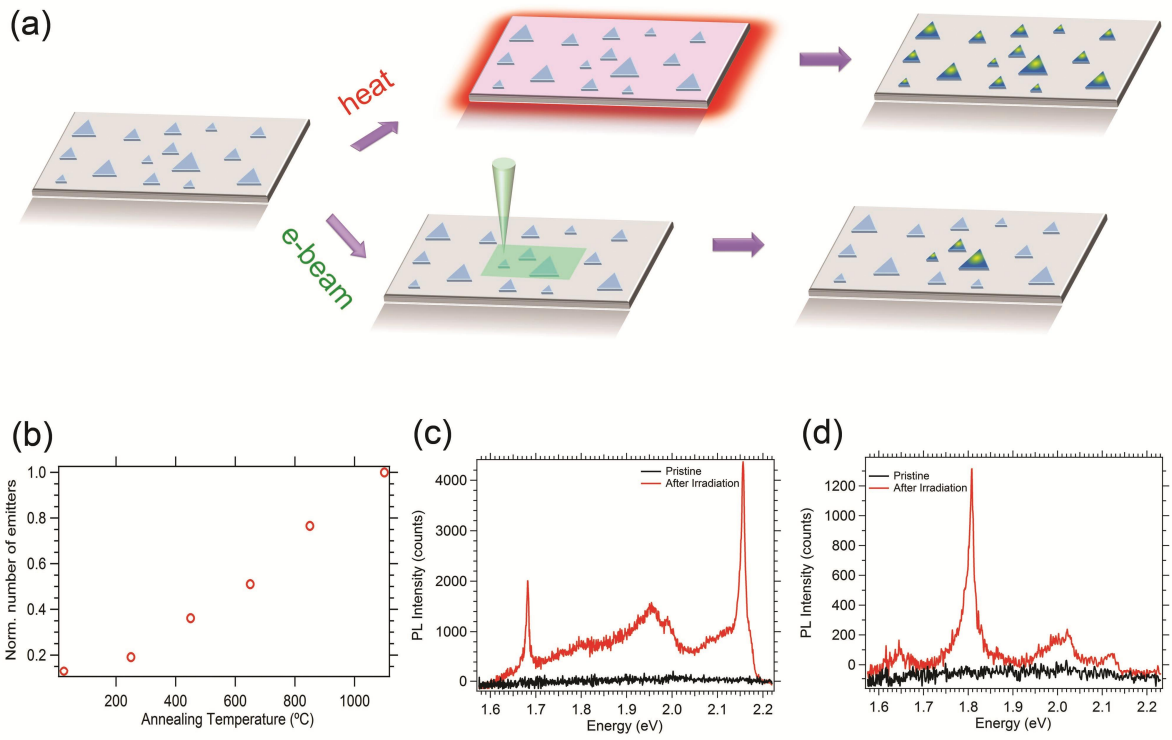

Figure 1. (a) Schematic illustrating the formation of emitters in hBN via annealing and electron beam irradiation. As-grown, dropcast hBN flakes are either annealed in an argon environment, or irradiated by an electron beam in a low vacuum H2O environment. (b) Shows normalized number of stable emitters found as a function of annealing temperature found in hBN nanoflakes. (c, d) Examples of PL spectra from emitters fabricated by an electron beam. Each pair shows data recorded from a fixed sample region before (black curve) and after (red curve) electron irradiation.[5]

Luminescent defects were also fabricated deterministically using electron beam irradiation in a scanning electron microscope. hBN nanoflake solution was first drop cast on a marked Si substrate, followed by pre-characterization of an

area of hBN flakes using confocal photoluminescence mapping and spectroscopy. The measurements were performed at room temperature using either a 532 nm continuous-wave (CW) laser, or a 510 nm pulsed laser as an excitation source for lifetime measurements as outlined in figure 2a. This same area then underwent irradiation by a 15keV electron beam in a H_2O vapor environment for 1 hour. The pre-characterized and irradiated regions were measured again, where figure 1c and d show a comparison of photoluminescence spectroscopy before and after electron irradiation from two regions. The spectra after irradiation (red curves in fig 1c and d.) indicate creation of defect formation through an electron beam mediated chemical restructuring of the hBN lattice as outlined in a previous study.[8] Consequently, no annealing procedure is needed for the formation of emitters using the electron beam, allowing for localized fabrication of defects in a one-step procedure.

3. MULTICOLOR EMISSION

Next, we characterize the narrowband multicolor emission from hBN, which spans across the visible and NIR region opening up the possibility of bio sensing and biolabelling applications. Figure 2a shows a simplified schematic of the confocal photoluminescence (PL) setup used to characterize hBN. A photoluminescence survey was conducted to collected spectra of various single defect centers in hBN (which was annealed previously in argon at 850°C). A representative range of room temperature PL spectra is shown in Figure 2(b, c). The emitters shown have narrow zero phonon lines (ZPLs) at a wide range of energies in the range of ~1.6 – 2.0 eV (~ 565 – 750 nm). A set of nine emitters are shown for clarity, however the range and variation in photon energy found is much greater as shown in the histogram in figure 2d.

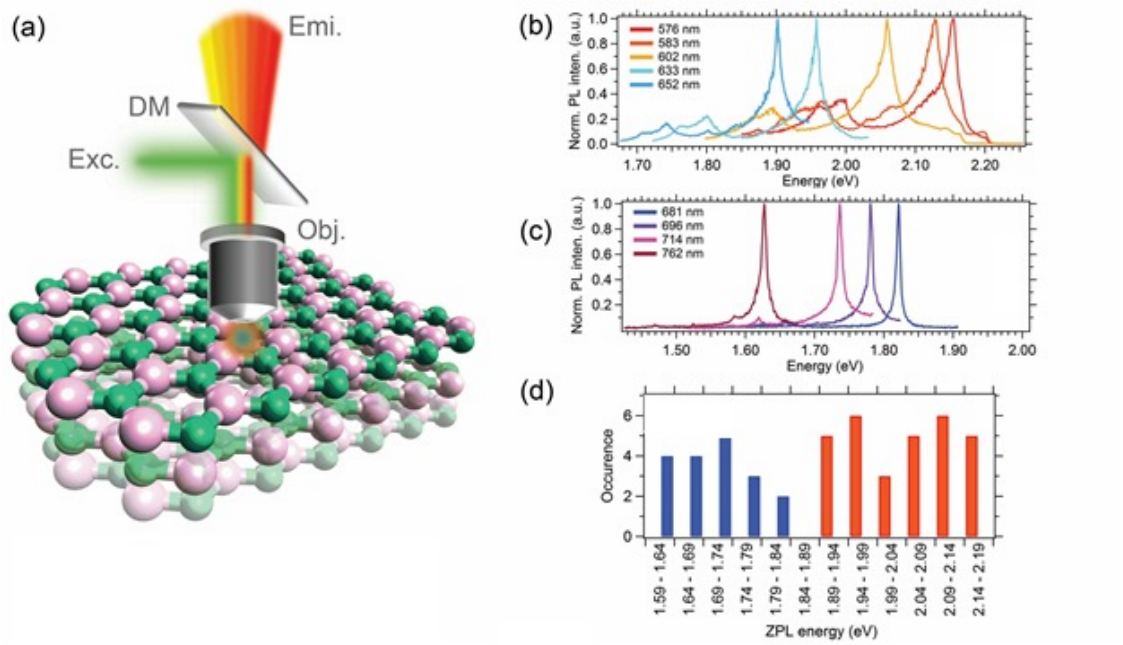

Figure 2 (a) Simplified schematic of the photoluminescence setup showing the excitation and emission of a defect center in a hBN lattice. The objective lens, dichroic mirror, excitation source and emission are denoted by Obj., DM, Exc., and Emi., respectively. (b) and (c) show nine examples of multicolor photoluminescence from point defects in hBN spanning a wide energy range (d) Histogram of ZPL energy for numerous emitters found in hBN. Figure modified from previous study.[5]

4. EMITTER STABILITY

To study of the stability of created emitters, we compared their spectra before and after subjection to different gaseous environments. hBN nanoflakes were annealed at 850C in Ar environment to promote the creation of emitters. Emitters were then chosen with a large difference between photon energies and compared their spectra before and after subjection to different gaseous environments (two examples are shown in figure 2a and c). The emitters were then characterized with confocal mapping and spectroscopy, annealed sequentially at 500°C for one hour each in hydrogen, oxygen and ammonia environments, and re-measured confocal mapping and spectroscopy after each annealing step.

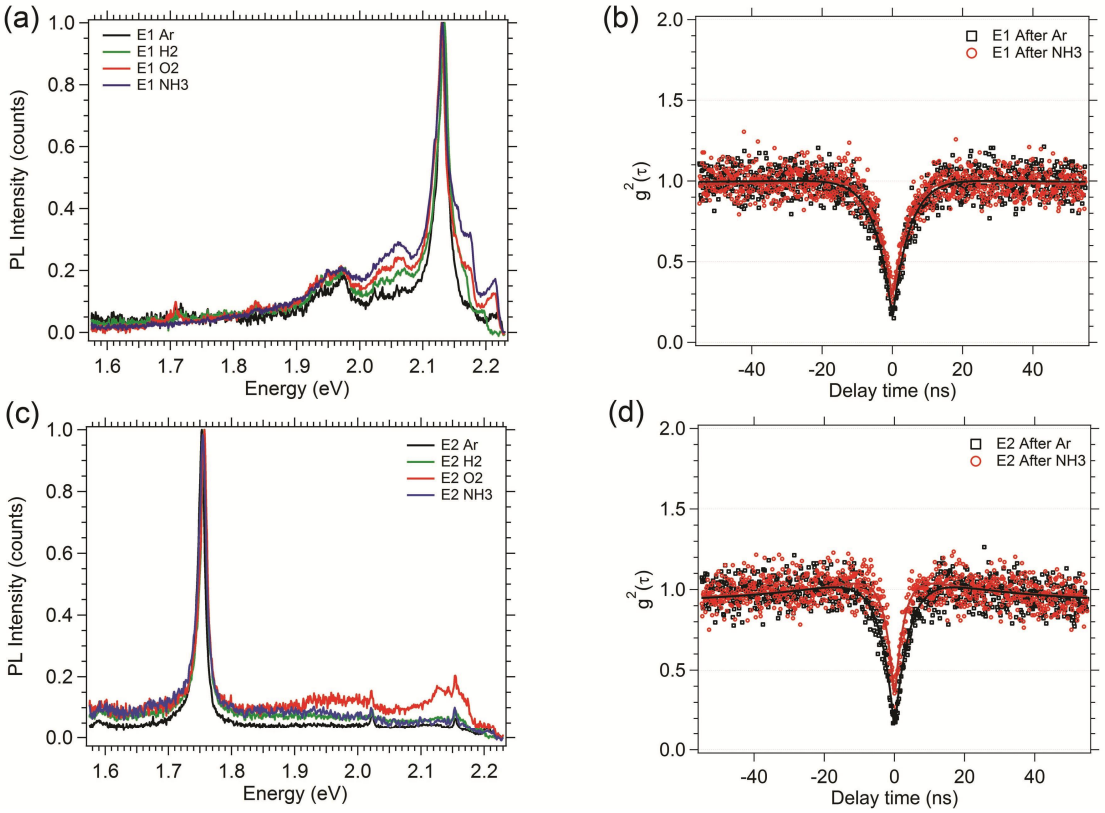

Figure 3. Stability of the emitters. (a,c) Normalized luminescence recorded at room temperature from two emitters (E1 and E2) after sequential annealing in argon, hydrogen, oxygen and ammonia. (b, d) Corresponding antibunching measurements proving that the quantum nature and lifetime of the defects persists after the sequential set of 30 min anneals performed in H_2, O_2 and NH_3 environments. Emitters E1 and E2 belong to Group 1 and 2, respectively.[5]

As can be seen in figure 2, there is no change in fluorescence intensity, suggesting that the tested emitters show extreme stability and chemical inertness even under reducing or oxidizing conditions at elevated temperatures. A Hanbury Brown and Twiss (HBT) setup was used to verify single photon emission from these defects. Figure 3b and d shows second-order autocorrelation functions ($g^{(2)}(\tau)$) before and after all annealing treatments which also highlights the robust quantum nature of the defect and the excited state lifetime of the emission source.

5. CONCLUSION

In conclusion, we present two methods to engineer room temperature multicolor single photon emission, based on annealing and electron beam irradiation. WE also show that the emitters are stable even after annealing in harsh environments such as oxygen, hydrogen and ammonia. The emitters exhibit narrow line widths of sub 10 nm at room temperature, and a short excited state lifetime, and high brightness. These properties enable the emitters to be distinguished and detected via both differing emission wavelengths and lifetimes, and can be exploited for biosensing, cellular imaging and biolabeling applications.

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