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Single-Photon Emitters in Boron Nitride Nanococoons

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Supporting Information

ABSTRACT: Quantum emitters in two-dimensional hexagonal boron nitride (hBN) are attractive for a variety of quantum and photonic technologies because they combine ultra-bright, room-temperature single-photon emission with an atomically thin crystal. However, the emitter's prominence is hindered by large, strain-induced wavelength shifts. We report the discovery of a visible-wavelength, single-photon emitter (SPE) in a zero-dimensional boron nitride allotrope (the boron nitride nanococoon, BNNC) that retains the excellent optical characteristics of few-layer hBN while possessing an emission line variation that is lower by a factor of 5 than the hBN emitter. We determined the emission source to be the



nanometer-size BNNC through the cross-correlation of optical confocal microscopy with high-resolution scanning and transmission electron microscopy. Altogether, this discovery enlivens color centers in BN materials and, because of the BN nanococoon's size, opens new and exciting opportunities in nanophotonics, quantum information, biological imaging, and nanoscale sensing.

KEYWORDS: Zero-dimensional material, hexagonal boron nitride, boron nitride nanococoons, single-photon emitter, quantum probe

S olid-state sources of single photons have broadly impacted the development of quantum technologies due to their robustness to ambient conditions¹⁻³ and ease of integration with on-chip devices.⁴ These attributes have allowed the realization of applications from quantum computers⁵ and entanglement between remote qubits⁶ to thermometry² and imaging³ in living biological systems. Recently, single-photon emitters (SPEs) in two-dimensional (2D) hexagonal boron nitride (hBN) have attracted significant attention because of their extreme brightness, photoluminescence (PL) stability,⁷⁻ and robustness to harsh chemical and temperature conditions.^{9,15} In addition, their nanometer-scale thickness allows for strong coupling to the environment or to photonic structures. However, hBN SPEs suffer from an emitter-toemitter wavelength variability of 200 nm,9 which proves detrimental to many applications in photonics, quantum information, and fluorescence imaging because of a strict reliance on a fixed and well-defined wavelength. Experimental evidence and theoretical analysis indicate that strain is an important contributor to this wavelength variation.9,12 Therefore, the variation can originate from morphological features

such as folds and wrinkles, or incidental bending or tensioning of the hBN sheet, factors that are challenging to control.

Because of the otherwise excellent properties of hBN, a means to reduce the strain-driven wavelength variability would propel the potential of the hBN SPE. One solution would be to utilize a geometry that is resistant to bending. Thick, bulk hBN samples have a large bending stiffness, and SPEs in such samples do possess a narrower emission wavelength range $(\sim 30 \text{ nm}^{16})$ relative to thin hBN sheets. However, this tighter emission range broadens considerably when the thickness of the sample is reduced to less than 100 nm,⁹ even with the small lateral scale of an hBN nanoflake. Thus, despite the improved SPE emission properties of bulk hBN, these properties cannot be combined with the desirable benefits of a nanoscale structure.

The boron nitride nanocoon (BNNC) is a ball-like, zerodimensional (0D) BN allotrope that possesses both a nanoscale

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size and a stable, rigid mechanical structure. The BNNC, which is structurally similar to a carbon buckyball fullerene,¹⁷ is composed of fully closed, nested BN polyhedra and provides more rigidity and fewer motional degrees of freedom than a 2D flake. This resistance to bending would result in lower wavelength variation of SPEs in this nanostructure. In addition to bending resistance, the BNNC also has a nanometer size (~1–100 nm), which would allow embedded SPEs to retain the efficient coupling of 2D hBN and to serve as sensitive probes of small systems. Critically, the BNNC has facets consisting of many flat, stacked layers or walls of BN (see Figure 1) that possess a local crystal structure identical to 2D



Figure 1. (a) High-resolution transmission electron microscopy (TEM) image of a BNNC on a BNNT showing its walls and hollow interior. (b) A sketch of a BNNC cross-section emphasizing the locally flat faces.

and 3D hBN.^{18,19} This structure imparts a large bandgap,^{20,21} as seen in other BN allotropes, and therefore permits the formation of deep-bandgap visible-range SPEs.

Despite the potential for BNNCs to support SPEs with a more-consistent, well-defined emission wavelength and the advantages of its nanoscale structure, the BNNC has yet to be investigated as a source of SPEs. Here, we examine a purified sample of BNNCs for the PL signatures of SPEs and determine if the prospective SPEs possess reduced emission wavelength variation. By using confocal optical microscopy, we discovered bright, stable SPEs that emit in the visible range and are active at room temperature and in air. These SPEs are stable over many days of continuous probing and, most notably, can possess a wavelength variation of 39 nm. By cross-correlating confocal optical microscopy with high-resolution electron microscopy, we determined that the SPEs exist in isolated BNNCs and, more often, in large aggregates of composite BNNC material.

Methods and Materials. The BNNCs used in this study were grown from boron feedstock in an inductively coupled plasma at high pressure.¹⁹ This commercially scalable process produces a mixture of BNNCs and BN nanotubes (BNNTs) but was tuned to preferentially produce BNNCs. The use of a boron source material minimized 2D or bulk hBN material in the synthesis product. The synthesis process also created boron nanocrystals, some of which were encapsulated by the BNNCs. We used a nitric acid treatment to remove these impurities. BN's excellent inertness²² protected the material from oxidative damage of the acid.

After treatment in nitric acid, the material was suspended in ethanol, sonicated, filtered at 200 nm, and resuspended.

Filtering helped remove larger assemblages of BNNC and BNNT or potential hBN sheets. For transmission electron microscopy (TEM) studies, the BNNCs were then drop-cast onto a lacey carbon TEM grid. This dispersion decreased the density of material to make it more likely to find isolated SPEs and to allow for cross-correlation characterization of the SPE host material. A TEM image of a BNNC can be found in Figure 1a with a sketch of the cross-section in Figure 1b. To create and increase the density of SPE defects, we used an FEI Helios dual-beam focused ion beam (FIB) and scanning electron microscope (SEM) to selectively irradiate the sample with 10 keV gallium ions at a dose of 10^{-14} C/ μ m². Subsequently, we annealed the samples in argon at 1 Torr and 750 °C for 30 min.¹⁴ To expedite sample processing, some samples were only annealed, which resulted in a lower defect density and defects with diminished stability.¹⁴

We used a custom-built scanning confocal microscope to generate two-dimensional fluorescence images of our samples. From these images, we identified areas with localized PL as potential SPEs. Typical scan areas were 10 μ m × 10 μ m. A schematic of this optical setup can be found in Figure 2e. This setup uses a 100× NA = 0.7 objective to focus light on our sample, a mode-filtered 532 nm laser for excitation, and avalanche photodiodes (APDs) for single-photon counting. The positioning of the laser focus has closed-loop control and nanometer-scale resolution in all three dimensions. When probing single SPEs, we implemented a PL feedback loop to compensate for sample drift. All measurements were taken in air and at room temperature. For the majority of our imaging, we kept the excitation power low (~20 μ W) to minimize damage to the lacey carbon.

We identified SPEs and their hosts by using a combination of confocal microscopy, time-correlated single photon counting, and high-resolution electron microscopy. A typical confocal image of the BNNC material on a TEM grid is shown in Figure 2a; an SPE is circled in white. We identified PL sources as SPEs (that is, whether they emit single photons at a time) by measuring the second-degree correlation function, $g^2(t)$, with a Hanbury-Brown-Twiss photon detection setup integrated with our scanning confocal microscope (see Figure 2e). To determine the morphology of the SPE host material, we correlated confocal images with SEM and TEM images. The grid lattice and local features of the lacey carbon of the TEM support facilitated imaging in the same regions for crosscorrelation. An SEM-FIB was used for coarse identification of the material, as shown in Figure 2b,c. For finer characterization, we used high-resolution TEM (obtained with an FEI Titan operated at 300 keV and an FEI Tecnai operated at 80 keV.) A representative TEM image of a single BNNC is shown in Figure 1a.

Results and Discussion. Confocal imaging revealed areas of bright, localized fluorescence. Three such bright regions are indicated by circles in Figures 2a and 3a. SEM and TEM imaging (discussed in more detail below) shows that these same optically bright regions contain large amounts of BN material, as shown in Figures 2b and 3b. Comparing the confocal and SEM images, we see some fluorescence from the lacey carbon support, but the intensity of this fluorescence is far below the signal in regions containing BNNCs.

By measuring $g^2(t)$ of localized PL sources, we detected the presence of numerous SPEs in the BNNC material. The $g^2(t)$ data for the PL source pictured in Figure 2a-d is shown in Figure 2f. We fit our $g^2(t)$ data to a model for a three-level



Figure 2. (a) Confocal image of a BNNC that hosts a SPE with an arbitrary intensity scale. The bright spot circled in white is a SPE hosted by a single BNNC. The bright spots circled in color were used as references to help correlate confocal and SEM and TEM images. (b) Low-magnification SEM image of the BNNC that hosted a SPE on lacey carbon. (c) High-magnification SEM image of the same BNNC on lacey carbon. (d) TEM image of the BNNC on lacey carbon showing the hollow interior and thick walls. (e) Sketch of our confocal microscope optical setup with two avalanche photodiodes in a Hanbury–Brown–Twiss setup for $g^2(t)$ measurements. (f) $g^2(t)$ for a single BNNC showing that $g^2(0) = 0.25$, proving it is a SPE.



Figure 3. (a) Confocal image of aggregated BN nanomaterial on lacey carbon with an arbitrary intensity scale. The bright spot circled in white is an SPE hosted by a cluster of BNNC. The bright spots circled in color were used as references to help correlate between confocal and SEM and TEM images. (b) Low-magnification TEM image of aggregated BN nanomaterial on lacey carbon. (c) High-magnification TEM image of the SPE-hosting aggregate material showing the large number of BNNCs present. (d) $g^2(t)$ for this material with $g^2(0) = 0.44$, proving it is a SPE.

system with a long-lifetime nonradiative transition: $g^{2}(t) = 1 - (1 + a)e^{-|t|/\tau_{1}} + ae^{-|t|/\tau_{2}}$ where τ_{1} is the radiative lifetime, τ_{2} is the nonradiative lifetime, and *a* is the amplitude of bunching. This model of a three-level-system is consistent with our data and has also been used to describe SPEs in hBN.^{7,16} We found the dip at a zero time-difference for this emitter to be $g^{2}(0) = 0.25$, well below the 0.5 threshold for a single photon source. In total, we found 23 SPEs, with excited-state lifetimes in the range 0.8–11 ns, and bunching amplitudes from 0 to 1. A large bunching amplitude (~1) indicates a long-lived non-radiative decay pathway.⁸ In addition, we found several dozen separate instances of antibunched PL (i.e., $0.5 < g^2(0)<1$.) We found roughly one SPE per 50 μ m × 50 μ m area.

We further characterized the SPEs by measuring their PL spectra at room temperature. These measurements were performed in a commercial Witec Raman spectrometer.



Representative spectra are shown in Figure 4a; these spectra have a strong, sharp peak and a broader, red-shifted shoulder

Figure 4. (a) Representative spectra for different SPEs with a range from 564 to 603 nm, normalized for clarity. The box and swarm plots summarize the ZPL data of spectra obtained. (b) PL intensity vs power curve showing I_{∞} = 320 kcps and P_{sat} = 1.5 mW. (c) Polarization vs PL intensity with a shape characteristic of a linearly polarized optical dipole and misalignment between the excitation and emission dipole.

that resemble the zero phonon line (ZPL) and phonon sideband, respectively, expected for a solid-state color center (additional spectra can be found in the Supporting Information). Across 12 distinct SPEs with strong ZPLs, we found an average ZPL of 578 \pm 14 nm with a total range of 39 nm, which is a factor of 5 lower than the range of 200 nm for emitters in few-layer hBN.^{9,13} The range seen in BNNCs is closer to the 30 nm ZPL range of SPEs in bulk hBN,¹⁶ and some measured spectra have ZPLs that are tightly grouped about an emission line at 567 nm. The deviation within this group (composed of all emitters below the median of 575.7 nm) is about ± 3 nm or a factor of 33 lower than few-layer hBN, suggesting a possible route toward further wavelength stability in this system. We can understand the small variability by considering the increased rigidity of the cocoon structure, which prevents strain-induced wavelength shifts, much like what occurs in bulk hBN. The phonon sideband is separated from the ZPL by 158 ± 15 meV, roughly consistent with 2D and bulk hBN SPEs.^{7,9,10,16} This energy separation is close to a peak in hBN's phonon density of states at 165 meV,²³ which provides evidence that the crystal structure of the BNNC near the SPE is similar to 2D and bulk hBN, as illustrated for the BNNC in Figure 1a. Despite the similarities to bulk hBN, the BNNC spectra are blue-shifted by ~20 nm relative to those in bulk hBN, a shift that may be caused by the different strain and bonding environment of the BNNC.

To gain further understanding of the SPEs excitation and emission properties, we examined the polarization dependence of their PL intensity. We found the two-lobed shape typical of an optical dipole as well as misaligned excitation and emission dipoles. We confirmed the dipole characteristic of these emitters by fitting the PL intensity versus θ data to the $\cos^2\theta$ shape expected for a linearly polarized dipole; see Figure 4c. Misalignment between emission and excitation dipoles was common although the angle between them varies. This misalignment can be attributed to indirect excitation of the emitter through a higher-lying state. Such misaligned excitation and emission optical dipoles are also found for SPEs in other BN allotropes.^{8,24}

We determined the brightness of these SPEs by measuring the PL intensity at various levels of incident power, as seen in Figure 4b. The polarization was adjusted in these measurements to maximize the PL intensity. We fit the data using a first-order saturation model,¹⁶ with an equation of the form $I(P)=I_{\infty}P/(P + P_{sat})$. For the brightest emitter suspended on lacey carbon, the saturation intensity, I_{∞} , was 318 kcps, and the saturation power, P_{sat} , was 1.48 mW.

The saturation intensity of our brightest emitter is an order of magnitude less than the 4000 kcps reported brightness of SPEs in 2D hBN.^{7–14} We can partially attribute the dimmer emission to a lower collection efficiency in our optical setup. At the same incident power, we found that a SPE in an hBN flake, prepared from commercially available hBN nanoflakes (Graphene Supermarket), had a PL intensity of 500 kcps, while a SPE in a BNNC had a PL intensity of 100 kcps. Accounting for the inefficiencies in our optical setup, we find that SPEs in BNNCs are dimmer by roughly a factor of 5 than those in hBN flakes. The remaining difference in brightness may be due to the low layer number of these structures, local crystalline damage, or the subwavelength size and high index of refraction of the BNNCs.^{25–27}

During optical characterization, we noticed a reversible reduction in brightness of some SPEs that remained stable on a time scale of minutes to hours. After further investigation, we found that extended illumination of some SPEs at high incident powers (i.e., at or above saturation, 1.5 mW) could induce a change from a bright to a dim state, with the overall PL intensity dropping by over 60%. This dimming was accompanied by a dramatic reduction of the ZPL intensity by over 80% (Figure 5a). In addition, we measured $g^2(t)$ for both the bright and the dim state and found a reduction in lifetime



Figure 5. (a) Spectra for the bright and dim state showing a reduction in ZPL and overall PL intensity without a corresponding change in wavelength, with intensity normalized to the ZPL of the bright state. (b) $g^2(t)$ for the bright state. The lifetime was 2.59 ns and $g^2(0) = 0.34$. (c) $g^2(t)$ for the dim state; the lifetime was 0.83 ns and $g^2(0) = 0.38$.

from 2.59 to 0.826 ns, shown in panels b and c of Figure 5, respectively. However, the SPE anti-bunching behavior persisted in the dim state. The lifetime change accompanied by the change in spectrum seems to suggest a change in the strength of phonon coupling or other nonradiative decay pathways.

The photoinduced changes we observed have pronounced differences from those seen in 2D hBN.¹¹ In 2D hBN, photodynamic processes were only observed under 405 nm illumination and primarily consisted of spectral diffusion, sometimes accompanied by dimming of the defect. In contrast, we observed dimming without spectral diffusion under 532 nm illumination. Also, the photoinduced changes in 2D hBN were stable on time scales of seconds, whereas we observed stability on the order of hours to days. It is possible that the photoinduced dimming and lifetime changes are due to a similar mechanism as proposed for 2D hBN, such as changes in the charge state of the SPE or surface desorption of oxygen.¹ However, the differences suggest that the photodynamics are unique to the BNNC structure and could be due to mechanical buckling or photochemical reactions at the highly strained and reactive edges of the BNNCs.

We used confocal and SEM and TEM cross-correlation to ascertain the morphology and identity of the SPE host material. Examples of these correlations can be found in Figures 2 and 3, where the PL source circled in white is an SPE and the areas circled in purple and orange are local features used to facilitate cross-correlation between optical and electron microscopes. The source of localized PL shown in Figure 2a (white circle) possessed an anti-bunching correlation of $g^2(0) = 0.25$, firmly establishing the emitter as an SPE. SEM and TEM images of the region near this SPE (Figure 2b-d) show a single particle of diameter ~150 nm. The SEM shows the particle has some depth (i.e., it is not flat) and has sharply angled facets in all three dimensions. TEM of the particle shows dense material (darker) at the edges of the particle and less material (lighter) at its center, consistent with the geometry of a hollow BNNC. The structure of a nanococoon and its sharply angled facets can be more clearly seen in Figure 1a, where the walls of the BNNC are resolved. The BNNC cluster seen in Figure 3c also exhibits the hollow-core and dense wall structure of nanococoons. Based off this collective evidence, we conclude that the SPE highlighted in Figure 2 exists within a single BNNC. The majority of the SPEs were found in aggregated mixtures of BNNC and BNNT material primarily composed of nanococoons (see Figure 3b,c and the Supporting Information.) Although the material is a mix of BNNCs and BNNTs, we note that isolated or bundled nanotubes lacked PL of any kind. This absence of PL from BNNTs agrees with other searches for SPEs in composite BN nanomaterial containing nanotubes.² Therefore, we suspect the SPEs were hosted by BNNCs alone. The apparent preference of SPEs to form in aggregated material is likely due to the larger amount of material available to host the emitter. Isolated BNNCs that possess an SPE also tend to be larger (~100 nm), thereby increasing the likelihood of containing an SPE. We point out that in all our TEM observations, we did not see any 2D or 3D hBN. Taken together, in addition to the noted differences in optical properties, we conclude that BNNCs are the hosts of all the SPEs measured in this work.

Conclusions. In this work, we have discovered bright, visible-wavelength SPEs in a nanometer-scale BNNC structure. These new SPEs were optically active under ambient

conditions, demonstrated stability over several days, and were found both in large isolated BNNCs and in clusters of BNNCs. While the lifetime, brightness, and PL stability of this SPE is similar to those in 2D hBN, it possesses one notable difference: its wavelength variation is smaller by a factor of 5 than SPEs in 2D hBN. This discovery advances the development of the ultrabright, stable solid-state single photon sources for quantum information, biological imaging, and photonics. Because the BNNCs can be synthesized in large quantities,¹⁹ they are viable for industrial-scale implementation. Because of their small size and emission wavelength stability, BNNCs can be incorporated into photonic structures, such as waveguides and photonic crystal cavities, that are of nanoscale size and designed around well-defined wavelengths. These same properties, in addition to the SPE's extreme brightness and established ease of chemical functionalization,^{29,30} make the BNNC ideal for tagging and tracking applications within living cells. The BNNC's closed structure may make the SPE wavelength sensitive to thermal strain, suggesting the use of BNNCs as a nanoscale temperature probe. The bright and dim photoswitching behavior of the SPEs, if due to interactions of the BNNC surface with the surrounding environment, could be combined with surface functionalization to enable a broad range of optically detected sensing applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.8b00632.

Additional details on the characterization of singlephoton emitter host materials. Figures showing singlephoton emitter spectra, confocal images, and SEM and TEM results. (PDF)

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The authors declare no competing financial interest.

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