Nanoscale axial position and orientation measurement of hexagonal boron nitride quantum emitters using a tunable nanophotonic environment

Pankaj K. Jha^{1,†}, Hamidreza Akbari^{1,†}, Yonghwi Kim^{1,†}, Harry A. Atwater^{1, 2, 3, *}

¹Thomas J. Watson Laboratory of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA 91125, USA.

²Resnick Sustainability Institute, California Institute of Technology, Pasadena, CA 91125, USA.
 ³Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA

91125, USA.

[†]*These authors contributed equally to this work.* **Corresponding author: Harry A. Atwater (haa@caltech.edu)* (Dated: July 15, 2020)

Color centers in hexagonal boron nitride (*h*BN) have emerged as promising candidates for single-photon emitters (SPEs) due to their bright emission characteristics and potential for high temperature operation, but precisely resolving emitter location is an important outstanding issue for many applications. While single-molecule super-resolution microscopy schemes can resolve emitter lateral position at the nanometer scale, complete determination of both axial position and three-dimensional dipole orientation (θ , ϕ) of these quantum emitters is a fundamental challenge. We report a method for determining both the axial position and three-dimensional orientation of SPEs in *h*BN by tuning the photonic local density of states, using a vanadium dioxide (VO₂) phase change material. Using this method, we were able to locate several specific quantum emitters at an axial distance of ~ 20 nm from the *h*BN/VO₂ interface while also determining their full dipolar orientation (θ , ϕ). Our approach may serve as a practical method to deterministically couple quantum emitters in *h*BN and other materials to photonic nanostructures, for applications in integrated quantum photonics.

Introduction

Point defects, such as vacancies, interstitial atoms or ions, and substitutional impurity atoms or ions, play an important role in determining the physical, electronic, and optical properties of solids (1). Over the past few decades, point defects that introduce electronic states with optical transitions, also known as color centers, have garnered great interest for quantum photonics applications, such as quantum computation and quantum information (2,3), quantum cryptography (4), and quantum sensing (5). Wide-bandgap materials, such as diamond (6), silicon carbide (7), gallium nitride (8), and zinc oxide (9) offer promising platforms for hosting quantum emitters with emission in the visible to near-infrared spectrum. However, these materials suffer from one or more intrinsic challenges such as a requirement for cryogenic temperatures, decoherence of emitted photons, optical coupling losses, and challenges associated with chip-based photonic integration. These problems have driven researchers to seek new candidate materials with fewer disadvantages (10,11).

Recent discoveries of quantum light emission from two-dimensional van der Waals (vdW) layered materials (12-17) have introduced promising candidates for single photon emitters (SPEs). In contrast to bulk materials, vdW materials offer easier integration with photonic structures and minimal loss due to refractive index mismatch (18, 19). Among several candidate vdW host materials, hexagonal boron nitride (hBN) has received particular attention due to its ability to offer a bright source of quantum light at room temperature. Remarkably, quantum emitters in hBN have shown high (> 80%) Debye-Waller factor (17), a brightness comparable to the brightest SPEs (10, 19), polarized emission (17, 20), giant stark shift (21-23), magnetic-field dependent quantum emission (24, 25), correlated cathodoluminescence and photoluminescence emission (26), and near transform-limited optical linewidth (27), all reported at room temperature. To date, the emission characteristics of hBN quantum emitters in multi-layered flakes are superior to those in monolayer flakes. For instance, a narrower zero-phonon line (ZPL), higher Debye Waller factor, and brighter emission (17, 28) are seen in multilayer hBN. However, the exact location of any quantum emitter within the thickness of any multi-layered hBN flake is unknown, whether randomly formed in natural crystals, grown by chemical vapor deposition or synthetically generated during sample processing (29-31). While super-resolution techniques have enabled nanometer-scale lateral (inplane) location of hBN quantum emitters (32, 33), their accurate location in the axial (vertical) direction is still an outstanding challenge.

In this Article, we demonstrate nanometer-scale axial location of *h*BN quantum emitters in a multi-layered flake by leveraging highly sensitive, distance-dependent modulation of the spontaneous emission lifetime of these quantum emitters when in close proximity to a tunable phase-change material, vanadium dioxide (VO₂). Specifically, we modify the local density of optical states (LDOS) by inducing an insulator-to-metal transition in VO₂ which in turn modulates the emission rate of quantum emitters near the *h*BN/VO₂ interface. This method, taken together with emission polarimetry to determine the three-dimensional (3D) orientation of the quantum emitter, give comprehensive information about emitters position and orientation. Measurement of *h*BN emitter location and 3D orientation with nanometer-scale resolution in multi-layered flakes (35) offer opportunities for both fundamental physics advances (36,37) and quantum photonic technologies (38,39).

RESULTS AND DISCUSSION

LDOS engineering with phase change material

The experimental configuration is shown in Fig. 1A. A quantum emitter is located at a distance d, within the thickness of an *h*BN flake, from the surface of a substrate that consists of a thin layer of VO₂ on sapphire. Photoluminescence excitation and detection were performed with optical pumping of quantum emitters by laser excitation from the top. The excited quantum emitter emission decay rate depends on its interaction with the optical environment (40). By optical environment we mean the substrate beneath and the air above the *h*BN flake. We model this interaction by treating the quantum emitter as an oscillating point dipole source oriented along the direction (θ , φ). For an emitter in an unbounded, homogeneous, and lossless medium with a refractive index *n*, the spontaneous decay rate is enhanced by a factor *n* compared to the free space. This result also holds true for bounded geometry as long as the emitter is at a distance $d \gg \lambda$ from any interface. When $d \ll \lambda$ the decay rate strongly depends on *d*, the dipole orientation (θ , φ), and the refractive index contrast across the interface (41-43). In this work, we manipulated the optical environment of a quantum emitter located in the vicinity of the *h*BN/VO₂ interface using VO₂ whose complex refractive index exhibits a sharp change when VO₂ is thermally switched from the insulating to metallic state, which occurs at near room temperature $T_c \sim 340$ K (44).

Figure 1B shows the calculated relative decay rate $\beta = \gamma_{Insulating} / \gamma_{Metallic}$ of an emitter as a function of distance d when the emitter is oriented perpendicular ($\theta = 0^{\circ}$) and parallel ($\theta = 90^{\circ}$) to the hBN/VO₂ interface. Here, $\gamma_{Insulating}$ and $\gamma_{Metallic}$ is the total (radiative and non-radiative) decay rate of the emitter when VO₂ is in insulating (30 °C) and metallic (100 °C) state respectively. In these simulations, we considered a flake thickness of 310 nm and an emission wavelength of 600 nm, corresponding to one of the quantum emitters in our experiment, shown in Figs. 4A and 4B. The refractive indices of the upper medium, hBN, and that of sapphire were set to 1, 1.82 (45), and 1.77 respectively. The complex refractive index of VO₂ at 600 nm was extracted from our ellipsometric data and was set to 3.05 + 0.42i and 2.57 + 0.64i for VO₂ in insulating and metallic state respectively. The thickness of the VO₂ layer was 40 nm. In general, the photoluminescence quantum yield (PLQY) of hBN quantum emitters varies in the range 0.6-1.0 (10,19) and a recent experiment has shown average PLQY in the range 0.6-0.8 for quantum emitters with zero-phonon line (ZPL) around 600 nm (46). The shaded area in Fig. 1 B, corresponds to this PLQY range. As can be seen, the relative modulation of decay rates for both orientations is clearly evident within first ~50 nm that quickly fades away at distances ~100 nm and above. We use this highly sensitive, distance-dependent decay rate of quantum emitters in the vicinity of the hBN/VO_2 interface to localize their position along the axial direction.

Figure 2 shows the individual contribution from radiative and non-radiative channels to the decay rates $\gamma_{Insulating}$ (Figs. 2 A, 2B) and $\gamma_{Metallic}$ (Figs. 2C, 2D) for both parallel and perpendicular orientations as a function of the distance (*d*) from *h*BN/VO₂ interface. The non-radiative decay rate of the emitter corresponds to the emission of a photon which is absorbed in the lossy material VO₂. Here, we considered the quantum yield of 0.7 which is typical of *h*BN quantum emitters with ZPL ~ 600 nm. Figure 2 illustrates that at distances in the range ~ 0-15 nm, decay rate γ is dominated by the non-radiative channel and thus the emitters located within this range of distances are "hidden" owing to a lack of light emission. However, the radiation contribution to the total decay rate is stronger for vertical dipole compared to the horizontal dipole within first ~50 nm with both states of VO₂. Thus, emitters found in the vicinity of *h*BN/VO₂ interface have a higher probability of dipole moment oriented along the vertical direction.

Characterization of *h*BN flake and VO₂ film

Figure 3A shows the optical microscope image of a thin *h*BN flake on a VO₂/sapphire substrate. This sample was prepared by mechanical exfoliation of high-purity *h*BN single crystals and transferred onto a 40 nm thick VO₂ film deposited on 500 μ m thick sapphire by pulsed laser deposition. In Fig. 3A, we can clearly see regions with different colors on the flake because of the interference contrast between regions of different thickness within the flake. To determine the thickness of this flake at each position, we employed atomic force microscopy (AFM). Figure 3B shows an AFM image of the *h*BN flake shown in Fig. 2A. The red dot in Figs. 3A, 3B indicates the location of the quantum emitters 'A', 'B', and 'C' with emission wavelength of 600 nm, 620 nm, and 570 nm respectively. Figure 3C show AFM height profile across the lines (S-E) indicated in Fig. 3B where flake thickness varies in the range 230-420 nm. At the location of the emitter 'A', 'B', and 'C' height of the flake is 310 nm, 340 nm, and 300 nm respectively.

The optical properties of insulating and metallic VO₂ used in the decay rate calculations (Figs. 1, 2A-D, 5D-F) and full-wave simulations (Supplementary Fig. S4) were characterized by spectroscopic ellipsometry for a VO₂ film mounted on a heated stage whose temperature was varied between measurements. The visible frequency refractive index, n, and extinction coefficient, k, of the VO₂ thin film in both insulating and metallic phases are shown in Supplementary Fig. S1. We clearly observe the switching of the optical constants of the VO₂ film when reaching the temperature triggered phase transition. It is worth noting that, n decreases in the wavelength range, while k increases as VO₂ undergoes an insulator-to-metal transition. To date, quantum emitters in hBN exhibit ZPL emission in the range 550-800 nm; thus, VO₂ is well-suited to modify the optical environment of hBN-based quantum emitters. We also investigated the morphology of VO₂ thin film on sapphire using AFM (Supplementary Fig. S3).

Characterization of hBN quantum emitters

Annealing in an inert environment is routinely used to create or activate quantum emitters in diamond (6) as well as hBN (18,19). For the hBN samples described here, we annealed a bulk crystal of hBN at 950 °C in a 1 bar pressure argon gas for 30 minutes before exfoliation. We mounted our sample consisting of hBN/VO_2 /sapphire on a Peltier heating stage capable of reaching temperatures up to 120 °C in a homebuilt confocal microscope configured to perform photon

intensity autocorrelation in a Hanbury, Brown and Twiss configuration, optical emission spectroscopy, and emission polarization measurements (Supplementary Fig. S2).

To locate the quantum emitters precisely, we performed confocal photoluminescence (PL) mapping in mode by which the sample was scanned point by point. Figure 4A shows a PL map over an area of 20 x 20 μ m² on the *h*BN flake. The location of the quantum emitters 'A', 'B', and 'C' are highlighted by dashed circles. The single photon emission nature of these quantum emitters is evident from their second-order autocorrelation measurements indicating $g^2(0) < 0.5$ (see Figs. 5A-C). Figures 4B-D show the PL spectra of these quantum emitters obtained for insulating and metallic VO₂. The emission spectra of each quantum emitter consist of a pronounced ZPL accompanied by a weaker phonon assisted emission. An increase in PL intensity at obtained for metallic VO_2 compared to insulating VO_2 is noticeable for all quantum emitters, which is indicative of a higher photon emission rate i.e. decrease in emission lifetime. This enhancement of emission rate is due to modification in LDOS owing to change in complex refractive index of VO₂ when switched from the insulating to metallic state. Recent experiment has reported that the decay rate of hBN quantum emitters remains constant even when heated up to 800 K (47) which further corroborates that the enhancement of decay rate is due to modification in LDOS rather than a thermal effect. The defect-based quantum emitter's dimensions are atomic scale, and thus lateral emitter size and location measurement is constrained by the optical diffraction limit (Supplementary Fig. S5).

Single-Photon characteristics of *h*BN quantum emitters.

To investigate the single-photon emission characteristics and decay lifetime of the quantum emitters, we measured their second-order intensity correlation functions $g^2(\tau)$ in both insulating and metallic phases of VO₂. In order to reduce the influence of background signal and noise, we corrected the raw $g_{raw}^2(\tau)$ using the function $g^2(\tau) = [g_{raw}^2(\tau) - (1 - \rho^2)]/\rho^2$, where $\rho = S/(S + B)$ where S and B refer to the signal and the background counts, respectively. This background corrected $g^2(\tau)$ was fitted with double exponential of the form (20)

$$g^{2}(\tau) = 1 - \rho^{2} \left[(1+\eta) e^{-\lambda_{1}|\tau|} - \eta e^{-\lambda_{2}|\tau|} \right]$$
(1)

where, η , ρ , $\lambda_{1,2}$ are laser power-dependent parameters (20,48). Here, λ_1 and λ_2 are the faster and the slower decay time constants, respectively, for a three-level system. The second-order intensity correlation functions $g^2(\tau)$ under continuous wave excitation pumping for the quantum emitters 'A', 'B', 'C' are shown in Fig. 5A, 5B, 5C, respectively, when VO₂ is insulating (blue dots) and metallic phase (red dots). The data for the metallic phase VO₂ configuration has been offset vertically for visual clarity. Equal-time coincidence counts $g^2(0)$ for each quantum emitter is less than 0.5, which indicates the presence of a single emitter. All measurements were performed at a constant 50 μ W pump laser power which is orders of magnitude smaller compared to the saturation power of ~ mW for hBN quantum emitters (10,18,19). From fitting our experimental data of correlation functions $g^2(\tau)$, we extracted the decay constants $(\lambda_{1,2})$ which has contributions from the spontaneous decay rates and the pump rate (48,49). The spontaneous decay rates (γ) of the emitters 'A', 'B', and 'C' are shown in the Table T1 (see supplementary information section S2 for details). From Table T1, we clearly see that for all the emitters, the decay rates are higher in the presence of a metallic-VO₂ when compared to an insulating-VO₂ configuration. Thus, the emitters 'A', 'B', 'C' is located at distances, from the surface of VO2, such that their optical environment is modified when VO₂ undergoes an insulator-to-metal transition.

To model the distance-dependence of the quantum emitter lifetime on VO₂ phase, we define the ratio of their decay rates in the insulating and metallic phases as β . Figures 5D-F show the twodimensional plot of relative decay rate β as a function of distance *d* from the *h*BN/VO₂ interface and the polar orientation angle θ of the dipole for each quantum emitters 'A', 'B', and 'C', respectively. Each plot has three contour lines; a dashed line for the relative decay rates β while the upper and the lower solid contour lines corresponds to the error in decay rate ($\pm \Delta\beta$). Using the experimental values of γ from the Table T1, we obtained the relative decay rates β for the quantum emitters 'A', 'B', and 'C' as $0.816 \pm 0.108, 0.798 \pm 0.124$, and 0.798 ± 0.062 respectively. From these simulations and the experimental values of β , it is evident that the quantum emitters are located within a narrow region at a distance $d \sim 20$ nm from the surface of *h*BN/VO₂ interface. However, the uncertainty in the axial position depends on the emitters' polar angle θ . For emitter 'A', uncertainty (full width) varies from ~ 13 nm at $\theta = 0^0$ to ~ 19 nm at $\theta =$ 90°. Similarly, for quantum emitters 'B' ('C') uncertainty in their axial location varies from ~ 14 nm (7 nm) to ~ 20 nm (7 nm) at $\theta = 0^0$ and $\theta = 90^0$ respectively.

Emission polarimetry and three-dimensional dipole orientation

Next, we focus on emission polarimetry of the quantum emitters. Previous studies (50) have shown that the three-dimensional orientation (θ, φ) of a dipole can be directly extracted by analyzing polarization characteristics of its emitted light. Figures 6A, 6D is the emission polarization measurement from the quantum emitters 'A' and 'B' respectively. The data is fitted by the function (50)

$$I(\alpha) = I_{min} + (I_{max} - I_{min})\cos^2(\alpha - \varphi)$$
(2)

where $I_{min, max}$ and φ are the fitting parameters. From the fit, we obtained for emitter 'A': $I_{min} = 0.356 \pm 0.013$, $I_{max} = 0.966 \pm 0.024$ and $\varphi = 175.7^{\circ} \pm 1.0^{\circ}$. Similarly, for emitter 'B': $I_{min} = 0.318 \pm 0.034$, $I_{max} = 0.888 \pm 0.066$ and $\varphi = 109.9^{\circ} \pm 2.9^{\circ}$. In emission polarimetry, the polar angle θ can be extracted from the degree of polarization of the emission defined as

$$\delta(\theta) = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} \tag{3}$$

From the fitting parameters (I_{max} , I_{min}), we obtained $\delta = 0.461 \pm 0.023$ and $\delta = 0.473 \pm 0.070$ for emitter 'A' and 'B' respectively. Figure 6B, 6E shows the calculated degree of polarization δ as a function of the polar orientation angle θ using the experimental values of numerical aperture (0.9), the refractive indices of *h*BN, VO₂ (insulating phase) and sapphire. The distance *d* of the quantum emitters 'A' and 'B' from VO₂/sapphire substrate was set to $d \sim 20$ nm. From Figs. 6C, 6F we clearly see that variation in the distance *d* is negligible (dashed line). The red dot in Figs. 6B, 6E represents the measured value of δ and we extract the polar orientation angle $\theta = 20.5^0 \pm 3.4^0$ and $\theta = 21.2^0 \pm 4.3^0$ for emitter 'A' and 'B' respectively. In estimating the value of error in θ we accounted for the error in location *d*, which is shown Figs. 6C, 6F by solid lines. Figure 6C represents nanometer-scale axial location of emitter A with an uncertainty (full-width) of ~ 15 nm, oriented along (θ, φ) = ($20.5^0 \pm 3.4^0$, $175.7^0 \pm 1.0^0$). Similarly, Figure 6F represents nanometer-scale axial location of emitter a with an uncertainty full-width of ~ 16 nm, oriented along (θ, φ) = ($21.2^0 \pm 4.3^0$, $109.9^0 \pm 2.9^0$). The strong vertical component of the dipole orientation for both emitters found in the vicinity of *h*BN/VO₂ interface are in agreement with our simulations results shown in Fig. 2. Such precise information about the position and

orientation of hBN quantum emitters, complemented by advances in accurate transfer techniques, would enable coupling of these emitter with nanophotonic structures (51,52).

Conclusions

We have demonstrated an experimental technique by which the axial position of quantum emitters in a multi-layered *h*BN flake can be extracted with nanometer-scale accuracy by exploiting the modification of photonic density of states using a phase change optical material, VO₂. Here, we tailor the optical environment of an emitter in the vicinity of VO₂/sapphire substrate which generates a sharply distance-dependent PL response. By performing time-resolved fluorescence spectroscopy, supplemented with emission polarimetry, several specific quantum emitters were identified at an axial distance of ~ 20 nm from the *h*BN/VO₂ interface while also determining their full dipolar orientation (θ , φ). It is worth noting that any phase-change material which experiences a sharp change in optical properties would be suitable for this purpose. However, VO₂ is particularly interesting because its insulator-to-metal transition happens near room temperature and is thus well suited to dynamically control emission rates of quantum emitters (*53,54*) near room temperature. Owing to the broadband nature of change in the dielectric function of VO₂ when switched from the insulating to metallic phase, our technique could also be extended to locating other visible or infrared quantum emitters (*10*).

Materials and Methods

Growth of VO₂ thin film on sapphire

A 40-nm thick vanadium dioxide (VO₂) film was formed on a cleaned c-plane single side polished sapphire substrate by pulsed laser deposition. A high-power pulsed laser beam vaporizes a vanadium target which deposits a thin film on the sapphire substrates in the presence of 5 m-Torr oxygen gas at an elevated temperature (650 °C). First, we confirmed that the surface of the VO₂ film grown on the sapphire substrate was uniform and continuous with root mean square roughness of around 1.5 nm that were measured by atomic force microscopy (Figure S8). The measurement result shows the morphology of the VO₂ film which consists of smooth and continuous small grains.

Optical characterization of hBN flakes

Optical characterization of samples was performed in a home-built confocal microscope capable of optical spectroscopy in visible range (Princeton HRS 300 system) and intensity auto-correlation measurement $(g_2(\tau))$ in a Hanbury Brown Twiss (HBT) configuration using a 50-50 beam splitter and two avalanche photo diodes (model). We used a fast scanning mirror (Newport) and a 4*f* telecentric configuration to perform photoluminescence mapping. The microscope uses a 532 nm CW laser (Cobolt) in order to pump emitters in *h*BN and a 100X objective (Leica) to focus the beam on the sample and used 50 µW power of laser (before objective) for all emitters. A quarter wave plate was put in the beam path at 45⁰ orientation with respect to linear polarization of laser in order to produce circularly polarized light. We pumped with circularly polarized light to excite all emitters irrespective of their in-plane dipole orientation. A tunable bandpass filter (Semrock versachrome) was used to only pass the zero-phonon line on the emitter into HBT setup to reduce background. Schematic of our optical characterization setup can be seen in Fig. S2.

Thermal measurements

Samples were mounted on a Peltier element to set their temperature. Samples were connected via a piece of copper tape to the Peltier element and the temperature of sample was controlled with a PID controller and a thermocouple attached to the surface of the Peltier element. The temperature was double checked with an IR thermometer to make sure the sample temperature is same as the controller temperature. We also measured the response of the Peltier element to measure how long it takes to reach the stabilized temperature (Fig. S3). Form room temperature to 100 C it takes less than 100 seconds but from 100 C to room temperature it takes around 1000 seconds, hence each time we waited 5 minutes when we were heating up and waited an hour when we were cooling down.

Finite element simulations.

Numerical simulations were performed using the commercial finite element software COMSOL Multiphysics for frequency domain electromagnetic full-field calculations. The simulation domain was truncated using perfectly matched layers. We modelled a quantum emitter as an electric point dipole source and calculated the spontaneous emission rate by probing the field at the location of the dipole. The non-radiative contribution to the decay rate was calculated by probing the heat generated in the lossy material (VO₂). The complex refractive index of VO₂ at the ZPL of emitters A, B, and C were taken from our ellipsometric data (Supplementary Fig. S1). The refractive index of *h*BN was set to be 1.82 at 600 nm, and a weak linear variation was employed to calculate refractive index at 570 nm and 620 nm as 1.84 and 1.81 respectively (45, 55). Sapphire has wavelength dependent refractive index (56).

We performed full-wave electromagnetic simulations using finite difference time domain methods to estimate the optimal thickness for a VO₂ film in order provide the largest optical contrast in the photoluminescence wavelength range. We used a commercial Lumerical finite-difference timedomain software package to obtain the reflectance spectra of the VO₂ film on a sapphire substrate. The reflectance maps of the thin film structure were monitored by varying the thickness of the VO₂ film for both insulating and metallic phases. Finally, the thickness of VO₂ film was optimized based on the FOM equation shown below. Fig. S3 represents the simulated FOM map, which indicates that about 40-nm-thick VO₂ film shows the largest reflectance contrast at the zero-phonon lines of our exfoliated *h*BN flake. Based on this analysis, we grew 40-nm-thick VO₂ films as explained in Section S8.

$$FOM = \frac{|R_{Metallic} - R_{Insulating}|}{R_{Metallic} + R_{Insulating}}$$

Here, *R_{Metallic}*: metallic phase reflectance and *R_{Insulating}*: insulating phase reflectance.

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Author contributions:

P. K. J, H. A, Y. K, and H. A. A conceived and developed the idea. P. K. J prepared the *h*BN flakes and performed AFM measurements. H. A performed the optical characterization of *h*BN flakes and correlation measurements. P. K. J and H. A performed emission polarimetry of *h*BN quantum emitters. Y. K prepared VO₂/Sapphire sample; performed ellipsometry, full-wave simulations, optical, and AFM characterizations of VO₂ thin films. P. K. J simulated the optical response of *h*BN quantum emitters and theoretical estimations with inputs from all co-authors. H.A.A. supervised all the experiments, calculations, and data collection. All authors contributed to the data interpretation, presentation, and writing of the manuscript.



Figure 1: Experimental schematic and distance-dependent modulation of relative decay rates. (A) Schematic of a quantum emitter in an atomically thin crystal of hexagonal boron nitride (*h*BN) located within the thickness of a flake on a substrate which consists of a thin layer of vanadium dioxide (VO₂) deposited on a sapphire crystal. (B) Relative decay rate $\beta = \gamma_{Insulating}/\gamma_{Metallic}$ as a function of distance *d* of a quantum emitter from the surface of VO₂ when switched from the insulating to metallic state. The blue and red curves refer to quantum emitters oriented parallel and perpendicular to the surface respectively and the shaded regions corresponds to the typical quantum yield range of 0.6-0.8 of *h*BN quantum emitters with zero-phonon line around 600 nm (*46*). For numerical simulation we considered the emission wavelength of 600 nm for the quantum emitter corresponding to the emitter 'A' (Fig. **4A**, **4B**). The refractive indices of the upper medium, *h*BN, and that of sapphire were set to 1, 1.82, and 1.77 respectively. The refractive index of VO₂ at 600 nm was set to 3.05 + 0.42i (insulating state) and 2.57 + 0.64i (metallic state) from our ellipsometric data (Supplementary Fig. S1).



Figure 2: Total $(\gamma_{total}/\gamma_0)$, radiative (γ_r/γ_0) , non-radiative (γ_{nr}/γ_0) , rates of spontaneous emission of a quantum emitter as a function of distance from VO₂ surface for two dipole orientation i.e. parallel ($\theta = 90^\circ$) and perpendicular ($\theta = 0^\circ$) to the surface. The emission wavelength is $\lambda_0 = 600$ nm corresponding to the emitter 'A'. (**A**, **B**) Insulating phase of VO₂, (**C**, **D**) metallic phase of VO₂. Free-space decay rate $\gamma_0 = n\omega_0^3 |\varrho|^2 / 3\pi\varepsilon_0 \hbar c^3$, with *c* being the speed of light, *n* the refractive index of *h*BN, ω_0 the atomic transition frequency, \hbar the reduced Planck's constant, and ϱ the amplitude of the dipole moment vector. The refractive indices of the upper medium, *h*BN, and that of sapphire were set to 1, 1.82, and 1.77 respectively. The refractive index of VO₂ at 600 nm was set to 3.05 + 0.42i (insulating phase) and 2.57 + 0.64i (metallic phase) from our ellipsometric data (Supplementary Fig. S1).



Figure 3: Characterization of the exfoliated flake. (A) Optical image of the mechanically exfoliated *h*BN flake on Sapphire/VO₂ substrate. (B) Atomic force microscopy image of the flake shown in (A). The red dots on the traces (S-E) in (B) and (A) indicate the position of emitters 'A', 'B', and 'C' with emission wavelength of 600 nm, 620 nm, and 570 nm respectively. (C) Line profiles along the region indicated by the trace in (B). At the location of the emitter 'A', 'B', and 'C' height of the flake is 310 nm, 340 nm, and 300 nm respectively.



scence (PL) map of the *h*BN flake on a substrate which consists of a thin layer of vanadium dioxide (VO₂) deposited on a sapphire crystal. The position of three single photon emitters is marked by white circles. The edge of the flake in marked by white dashed line. The PL spectra of emitters 'A', 'B', and 'C' shown in (**B**), (**C**) and (**D**) respectively were obtained with VO₂ in insulating state (blue) and metallic state (red).



Figure 5: Single photon source characterization and axial location in *h*BN flake. Plot of the second order photon correlation measurement, $g^2(\tau)$ for the emitters 'A', 'B', and 'C' in (A), (B) and (C) respectively. The experimental data, blue squares for insulating VO₂ phase and red stars for metallic VO₂, were fitted using Eq. (1) to obtain the decay rates of the emitters. From the fit, we calculated the relative decay rates $\beta = \gamma_{Insulating}/\gamma_{Metallic}$ for the three emitters 'A', 'B', and 'C' as 0.816 ± 0.108 , 0.798 ± 0.124 , and 0.798 ± 0.062 respectively. For clarity, $g^2(\tau)$ data obtained for metallic VO₂ in (A), (B) and (C) were shifted by 1, 1.5, and 1 respectively. Plot of the relative decay rates β as a function of the distance (*d*) from the surface of VO₂ and the polar angle (θ) for the emitters 'A', 'B', and 'C' are shown in (D), (E), and (F) respectively. The dashed contour lines in (D), (E), and (F) corresponds to the experimental value of β obtained from (A), (B), and (C) respectively, while the solid lines correspond to the error $(\pm \Delta \beta)$ in the ratio.



Figure 6: 3D-Orientation of *h*BN quantum emitters and nanometric axial location. (A, D) Polar plots of the photoluminescence (PL) intensity of the emitter 'A' and emitter 'B' respectively as a function of the emission polarization analysis angle (α). The PL data (solid spheres) were fitted using Eq. (2) to extract the azimuthal angle (φ) of the emitters and the degree of polarization (δ). From the fit, we deduce that for emitter A, $\varphi = 175.7^{\circ} \pm 1.0^{\circ}$; $\delta = 0.461 \pm 0.023$ and for emitter B, $\varphi = 109.9^{\circ} \pm 2.9^{\circ}$; $\delta = 0.473 \pm 0.070$. (B, E) Calculated value of degree of polarization (δ) as a function of the polar angle (θ) of the emitters located at a distance of ~ 20 nm from the surface of VO₂. The red dots in (B) and (E) corresponds to the experimental value of δ obtained from (A) and (D) respectively. The extracted value of the polar angle for emitter A and B are $\theta = 20.5^{\circ} \pm 3.4^{\circ}$ and $\theta = 21.2^{\circ} \pm 4.3^{\circ}$ respectively. (C, F) Purple shaded region shows the range of the distance (*d*) and the polar angle (θ) of the emitters 'A' and 'B' respectively based on our experimental data and simulations.

Emitter	Decay rate, $\gamma_{\text{Insulating}}$ (MHz)	Decay rate, $\gamma_{Metallic}$ (MHz)
А	245 ± 19	301 ± 33
В	693 ± 45	868 ± 122
С	274 ± 16	343 ± 18

Table 1: Spontaneous emission rates of emitters. Spontaneous decay rates of the emitters 'A', 'B', and 'C' in the vicinity of VO₂ in insulating phase and metallic phase. The decay rates are estimated based on the fitting of $g_2(\tau)$ and subtracting the contribution of pump-dependent excitation rate (see Supplementary section S2 for details).

Supplementary Materials for

Nanoscale axial position and orientation measurement of hexagonal boron nitride quantum emitters using a tunable nanophotonic environment

Pankaj K. Jha[†], Hamidreza Akbari[†], Yonghwi Kim[†], Harry A. Atwater^{*}

[†]These authors contributed equally to this work. ^{*}Corresponding author: Harry A. Atwater (<u>haa@caltech.edu</u>)

This PDF file includes:

Fig. S1. Complex refractive index of VO₂ in insulating and metallic phase
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Fig. S6: Temporal response of Peltier stage.

Section S1: Effective medium approximation

Section S2: Photophysics of *h*BN quantum emitters



Fig. S1: Complex refractive index of VO₂ in insulating and metallic phase. Extracted value of real (*n*) and imaginary (*k*) part of the complex refractive index of 40 nm thick layer of VO₂ deposited on sapphire crystal at 30°C (blue) and 100°C (red) from our ellipsometric data.



Fig. S2. Experimental setup. Schematic of the homebuilt confocal microscope used to characterize hBN quantum emitters and perform correlation measurements.



Fig. S3. Surface characterization of VO₂ film. Atomic force microscope measurement of VO₂ film deposited on a sapphire substrate. This result shows that the film is uniformly grown, and the root-mean-square roughness is around 1.5 nm (2 μ m × 2 μ m) which is much smaller than thickness of the film which is 40 nm.



Fig. S4. Optimization of VO₂ thickness. Figure of merit map (FOM) of a VO₂ film on a sapphire substrate obtained by full-wave simulations. The FOM indicates the reflectance contrasts between the insulating and metallic phases of VO₂. The results indicate that the largest optical contrasts at the zero-phonon lines when VO₂ thickness is about 40 nm.



Figure S5. Background subtraction for correlation measurements. Background subtraction for g^2 measurement of emitter B. (a) shows a PL map around the emitter, (b) shows a profile of the PL map shown by a dashed line in (a) with a gaussian fit to it, and values for signal and background. (c) shows g^2 result before background subtraction and (d) shows g^2 result after background subtraction.



Fig. S6. Temporal response of Peltier stage. Response of the Peltier stage as a function of time for ramp up and cooldown. Shaded region shows the ramp up region and the temperature is set to 100 C for 30 seconds and then the temperature decreases as a result of convection.



Fig. S7. Temperature-dependent reflectance spectra of a VO_2 film during the heating cycle (dotted lines) and simulated reflectance curves of the film using the Bruggeman effective medium theory (solid lines). We observe gradual reflectance variations upon phase transition in VO_2 , where the volume fraction of metallic phase VO_2 gradually evolves within the insulating phase VO_2 host.

Section S1: Effective medium approximation

In order to characterize the optical properties of the VO₂ film grown on a sapphire substrate, we measured reflectance spectra in the visible range. The temperature-dependent reflectance curves were measured by using a microscope spectrometer with an external heating stage. Figure S7 shows the temperature-dependent reflectance modulation in the 30–100 °C range of the 40-nm– thick VO₂ film for the heating cycle. We observed a gradual reflectance change as a result of the insulator-to-metal transition when we slowly changed the substrate temperature. The temperature-dependent curves represent a gradual decrease of the reflectance as the VO₂ film becomes a lower index and a more lossy metallic state.

Further, we employed the Bruggeman effective medium approximation to estimate the intermediate optical constants as a function of volume fraction of the metallic phase of the VO_2

layer (57). The legend R (0.00) denotes the purely insulating phase VO₂, while the legend R(1.00) represents the purely metallic phase VO₂. The estimated optical constants were used in full-wave simulations to monitor the reflectance values at normal incidence (Figure S4). The tendency of the full-wave simulation results is consistent with the measured spectra, which validates the refractive index and the thickness of the VO₂ film that we characterized.



Fig. S8: Three-level system with corresponding decay and excitation rates.

Section S2: Photophysics of hBN quantum emitters

We model single *h*BN quantum emitter as three-level system that consists of a ground state $|b\rangle$, excited state $|a\rangle$ and metastable state $|c\rangle$ as shown in Fig. S8. The emission characteristics of this quantum emitter can be described by rate equations for population of the three levels (48).

$$\dot{\varrho}_{aa} = R\varrho_{bb} - (\gamma_b + \gamma_a)\varrho_{aa} \qquad (S1)$$
$$\dot{\varrho}_{cc} = \gamma_a \varrho_{aa} - \gamma_c \varrho_{cc} \qquad (S2)$$

Here, *R* is the rate of excitation and γ_i (with i = a, b, c) is the decay rate of population (radiative and non-radiative combined). These equations are also supplemented with population conservation equation $\rho_{aa} + \rho_{bb} + \rho_{cc} = 1$. Using the rate equations, one can derive the analytical expression for the normalized "ideal" second-order autocorrelation function $g^2(\tau)$ as:

$$g^{2}(\tau) = 1 - \left[(1+\eta)e^{-\lambda_{1}|t|} - \eta e^{-\lambda_{2}|t|} \right]$$
(S3)

where the coefficients are given in the limit $(\gamma_b \gg \gamma_a, \gamma_c)$

$$\lambda_1 = R + \gamma_b \tag{S4}$$

$$\lambda_2 = \gamma_c + \frac{R\gamma_a}{(R + \gamma_b)} \tag{S5}$$

$$\eta = \frac{R\gamma_a}{[\gamma_c(R+\gamma_b)]} \tag{S6}$$

However, in the presence of a background such as laser scatter or diffused photoluminescence Eq. (S3) takes a modified form (20)

$$g^{2}(\tau) = 1 - \rho^{2} \left[(1 + \sigma) e^{-\lambda_{1}|\tau|} - \sigma e^{-\lambda_{2}|\tau|} \right]$$
(S7)

where, ρ quantifies the background and $g^2(0) = 1 - \rho^2$. The decay rate of the excited state $|a\rangle$ is $\gamma = \gamma_a + \gamma_b \approx \gamma_b$ as the transition rate to the metastable state $|c\rangle$ is orders of magnitude smaller compared to the decay rate γ_b . From Eq. (S4) we can obtain the decay rate of the quantum emitter using the pump-power-dependent spontaneous decay rate λ_1 as $\gamma = \lambda_1 - R$. The absorption rate is given by $R = \sigma_{abs} I/hv$ (49) with absorption cross-section σ_{abs} , excitation intensity I, and excitation frequency v. In our experiment, the focal spot was near diffraction limit (~ 0.5 μm), the average pump power was kept constant at $P_{avg} = 50 \ \mu W$ which is orders of magnitude smaller compared saturation power of ~ mW.