Single Defect Center Scanning Near-Field Optical Microscopy on Graphene

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ABSTRACT: We present a scanning-probe microscope based on an atomic-size emitter, a single nitrogen-vacancy center in a nanodiamond. We employ this tool to quantitatively map the near-field coupling between the NV center and a flake of graphene in three dimensions with nanoscale resolution. Further we demonstrate universal energy transfer distance scaling between a point-like atomic emitter and a two-dimensional acceptor. Our study paves the way toward a versatile single emitter scanning microscope, which could image and excite molecular-scale light fields in photonic nanostructures or single fluorescent molecules.

KEYWORDS: Scanning near-field optical microscopy, scanning probe, FRET, graphene, nitrogen-vacancy center, nanodiamond

Imaging the optical near field of nanosized structures is of fundamental interest to various areas of photonic, material, and biological sciences. This need has driven the development of several versatile near-field imaging methods, based on cathodoluminescence1 or scanning near-field optical microscopy,2 which have evolved into a routine technique with a resolution in the 10 nm range. A near field probe made from a single quantum emitter could enable qualitatively new measurements. Simultaneous measurements of its fluorescence lifetime and intensity would allow quantifying coupling efficiencies and near-field intensities,3 and its atomic size would push resolution by an order of magnitude. This would enable imaging even of extremely short-ranged interactions such as fluorescence resonance energy transfer (FRET), a nonradiative dipole–dipole interaction between transition dipole moments of a donor and an acceptor, which typically has a range of only a few nm. To achieve this elusive goal, different donors and acceptor systems have been used like single dye molecules4–7 or quantum dots,8,9 but most of these systems suffer from blinking or limited photostability, which has rendered their use cumbersome in practice and so far precluded the stable and quantitative observation of FRET with a scanning probe microscope.10 The only remedy to these problems so far has been operation at low temperature where single molecular fluorescence usually is stable.11 Recently, however, the nitrogen-vacancy (NV) center, an atom-like photon emitter in diamond, has emerged as a candidate for a more robust probe for near-field microscopy. It proves to be photostable even at room temperature,12 can be brought into nm proximity of any photonic system,13,14 and has been proposed as a stable emitter for near-field microscopy.15 As a result, FRET has been demonstrated between a stationary NV and a nearby single molecule with high transfer efficiency.16,17 Here, we demonstrate a scanning probe near field microscope based on NV centers and use this tool to investigate the FRET interaction of a single NV emitter with graphene.18–21 We demonstrate that a scanning NV center can be reliably navigated into the short-range of the FRET interaction (∼15 nm) and image FRET efficiency in all three dimensions with a resolution on the order of the FRET interaction range. This result opens a new way to probe and image relevant material properties like the local Fermi energy, which are predicted to modify the FRET intensity. It could equally yield a flexible source to deterministically inject plasmons at specific locations into graphene nanostructures.

All experiments use a home-built scanning FRET microscope based on an atomic force microscope (AFM) with an optically accessible tip. Single NV centers inside nanodiamonds on the tip of the AFM are used as FRET donors. A laser beam exciting the NV center is focused through the sample onto the NV. Fluorescence of the defect center is collected through the same tip of the AFM are used as FRET donors. A laser beam exciting the NV center is focused through the sample onto the NV. Fluorescence of the defect center is collected through the same AFM channel (see Figure 1). To allow for close proximity between the defect and graphene, small nanodiamonds with diameters around ∼25 nm containing single NV centers were used. When the NV center is placed in close proximity to the graphene sample, Förster energy transfer quenches its fluorescence with a much higher efficiency22 than the 2.3% absorption observed for a graphene monolayer in the far field.23 In this process, an electronic excitation of the NV center is nonradiatively transferred into an exciton in graphene (Figure 1b), which quickly dissipates excitation energy mostly by internal radiationless decay.24 Occurring at a rate $\gamma_{nr}$ this process...
The graphene transition dipole commonly known for point-like objects such as molecules or atoms. This distance dependence agrees with more elaborate theories, provided that $z$ is restricted to the near-field range, where the distance to graphene is larger than the lattice spacing, but still much smaller than the optical wavelength. 

Recently, it has been confirmed experimentally using quenching of fluorescent molecules separated from graphene by various spacers. 

Quantitatively, the Förster distance can be calculated from eq 2 and the expressions of $\gamma_{wu}$ and $\gamma_{f}$ stated in previous work to be

$$z_0 = \frac{\hbar c^3}{\sqrt{4.512(h\omega)^4v_0}} = 15.3 \text{ nm}$$

In the following, we discuss our scanning FRET experiments on layers of different graphene thickness. We acquired images in the lateral $(xy)$ dimensions (Figure 2c) as well as in a vertical $(xz)$ plane (Figure 2b). For the latter measurement, the AFM was operated in AC (tapping) mode, where the cantilever continuously oscillates and repeatedly touches the sample surface. A three-dimensional image was reconstructed by correlating the emission times of the recorded fluorescence photons with the phase of the oscillating cantilever. 

To compare eq 1 with results from Figure 2c, we transform the fluorescence $I(x,y,z)$ observed in measurements into a quenching rate $\gamma_{wu}(x,y,z)$ by the relation

$$\gamma_{wu} = \left( \frac{I_{0} - I_{\text{fl}}}{I(x,y,z)} - 1 \right) \gamma_{f}$$

where $I_{0}$ is the unquenched NV fluorescence intensity and $I_{\text{fl}}$ the fluorescence of the background. In all the following, we derive a radiative rate $\gamma_{r} = 1/\tau_{NV}$ based on the measured fluorescence lifetime $\tau_{NV} = 8.5$ ns of the NV on the tip. Note that this conversion implicitly assumes unity quantum efficiency.

In the case of Figure 2, the monolayer quenching rate was $78.4 \times 10^{6} \text{ s}^{-1}$ for a double layer $101.2 \times 10^{6} \text{ s}^{-1}$, and for several layers, $185.9 \times 10^{6} \text{ s}^{-1}$.

Thanks to their atomic size, scanning single emitters are able to map near-field couplings with molecular (nm) resolution in all three dimensions. As a first application of this remarkable property, we experimentally confirmed the theoretical model of eq 1. The result is shown in Figure 3. In the lateral dimensions (Figure 3a–c), a high-resolution scan of a graphene edge (Figure 3b, methods) reveals that fluorescence drops smoothly when the NV center is moved over the flake, with 68% of the decay occurring within a length of $\sim 24$ nm centered on the edge. This resolution of our imaging method is limited by the vertical separation between the NV center and the graphene flake. This distance is nonzero, even though the image was acquired in contact mode since the NV-center is located inside the nanodiamond at some residual height above its surface.

We quantitatively extract this distance by fitting the observed profile to theory (solid line in Figure 3c). This latter curve was obtained by numerically integrating eq 1, taking into account the fact that the NV transition has two orthogonal transition dipoles $\mu_{1}$ and $\mu_{2}$

$$\gamma_{wu}(x) = \left( \gamma_{wu}^{\mu_{1}}(x) + \gamma_{wu}^{\mu_{2}}(x) \right)/2$$

$$\gamma_{wu}^{\mu}(x) = A \mu_{g}^{2} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy |E_{P}(x,y)|^{2}$$
The remaining free parameters $A$, $\mu_g^2$, and $z_{NV}$ are fit to the data, and the dipole orientation is chosen as $\mu_1 || ez$, $\mu_2 || ex$ to best fit the observed behavior. The achieved resolution is limited by the spatial extent of the near-field $E_p$, which is of the order of the NV–graphene distance. Reverting the argument, we can extract this distance from the fit, finding that $z_{NV} = 15.9 \pm 0.4$ nm. As discussed above, we interpret this value as the distance between the NV center and the surface of the nanodiamond.

We also measured the vertical dependence $\gamma_{sv}(z)$ by repeatedly approaching and retracting the tip on a large graphene surface (Figure 3d). At a tip–sample spacing of about 8 nm (corresponding to $z_{NV} = 24$ nm), the tip rapidly snaps to the surface, so that no data could be acquired between this point and contact (15 nm). As for Figure 3c, we find that the data is well described by eq 1 and in particular agrees with the predicted $z^{-4}$ law of eq 2. Using the value $z_{NV}$ obtained from the lateral scan, we can quantitatively fit the data and infer a Förster distance of $z_0 = 14.5 \pm 0.4$ nm, in reasonable agreement with the theory prediction ($z_0 = 15.3$ nm, eq 3).

Summarizing, we have demonstrated optical scanning fluorescence resonance energy transfer microscopy with a single NV center in nanodiamond as emitter. We reliably placed this local probe sufficiently close to graphene to observe energy transfer as large as 40%. Our results confirm theoretical predictions and recent experiments, in particular the $z^{-4}$ dependence of the energy transfer rate between a point-like emitter and a graphene monolayer. Employing a single scanning emitter enabled us to map the transfer efficiency in all three dimensions without the need for any special preparation of the sample. With this technique, we have obtained nanoscale resolution SNOM images of arbitrarily shaped graphene flakes. This opens the way to image energy transfer into arbitrary nanostructures, such as structured graphene or carbon nanotubes. Furthermore, our method promises to map changes of material properties such as the Fermi energy in a contactless and noninvasive way by monitoring concomitant changes in the FRET efficiency. In another extension of the experiment, the scanning emitter could be used to inject single plasmons instead of excitons in other materials, e.g., silver nanowires or doped graphene. While graphene is an interesting photonic material in its own right, application of the technique to other nanophotonic structures and acceptors, e.g., single molecules, certainly would be of great interest. Applications in biological sciences are easily envisioned. Here, scanning FRET might become a valuable addition to other FRET based techniques for, e.g., imaging larger protein structures of cellular surfaces. Such methods may...
be combined with the magnetic field sensing capabilities of the NV center to yield a truly multifunctional local probe.

Methods. The setup used for the experiments is a home-built scanning confocal microscope combined with an atomic force microscope (AFM) (MFP-3D Asylum Research). We used a frequency doubled cw Nd:YAG laser (Coherent Compass) and, for the lifetime measurements, a pulsed fiber laser (Fianium). The excited and fluorescent light is collected by a high NA objective (Olympus PlanAPO, NA = 1.35), and the fluorescent light beam passes a dichroic beamsplitter (640 DCXR, Chroma) and a bandpass filter (650–750 nm) until it is detected in an avalanche photodiode (SPQR-14, Perkin-Elmer). The lifetime is measured by TCSPC electronics (PicoHarp 300, PicoQuant GmbH) and by SymPhoTime V4.0 software.

The nanodiamonds are brought onto commercially available cantilevers (NanoAndMore, PL2-NCHR) by an UV-curable glue (Thorlabs, NOA81).

To detect an image in the xz-plane, we used a field-programmable gate array (FPGA, OpalKelly XEM3005) that bins the arriving photons corresponding to the different heights of the oscillating tip. A custom software is used to generate a three-dimensional image.

The edge profile (Figure 3c) was obtained by averaging a two-dimensional scan (150 scan lines of Figure 3b) along the direction of the graphene edge.

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Notes
The authors declare no competing financial interest.

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