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Zero-phonon linewidth of single nitrogen vacancy centers in diamond nanocrystals

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Photoluminescence excitation spectroscopy of nitrogen vacancy (NV) centers in type Ib diamond nanocrystals shows that in spite of spectral diffusion and spin-nonconserving transitions, zero-phonon linewidth as small as 16 MHz, which is nearly lifetime limited, can be observed at low temperature. Relatively small effects of spectral diffusion have also been observed in a small fraction of NV centers.

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A nitrogen vacancy (NV) center in diamond consists of a substitutional nitrogen impurity and a carbon vacancy in an adjacent lattice site.[1] The exceptional spin properties of NV centers, including triplet spin states as the ground states, long-lived ground-state spin coherence, and efficient optical spin detection, have enabled optical control and coherent coupling of individual spins.[2–7] NV centers in diamond nanocrystals can also be incorporated in an optical microresonator. Signatures of strong-coupling cavity QED have been recently reported in a cavity QED system, in which NV centers in diamond nanocrystals are coupled to whispering gallery modes in a silica microresonator.[8]

Optical properties of NV centers, however, are less well understood.[9,10] Optical transitions in a NV center are complicated by photoionization of nitrogen impurities.[11] The ground state of substitutional nitrogen impurities in diamond is approximately 1.7 eV below the conduction band of diamond. Since the transition energy for the zero-phonon line of a NV center is 1.95 eV, resonant excitation of the NV center can photoionize nearby nitrogen impurities. Fluctuating charges in the conduction band of diamond can subsequently lead to additional broadening or spectral diffusion of optical transitions in the NV center. In addition, the energy level structure of a NV center is also complicated by the presence of strain in diamond. While the ground state of the NV center features a triplet spin state, the strain along with spin-orbit interactions modifies the excited states, which can lead to enhancement of nonspin-conserving transitions that are otherwise nearly dipole forbidden.[5]

Recent experimental studies have shown that single NV centers in high purity type IIa bulk diamond can exhibit a lifetime-limited excitation linewidth as small as 13 MHz.[12] In comparison, studies of single NV centers in synthetic type Ib diamond, which has a high concentration of nitrogen impurities, have shown linewidth exceeding 100 MHz.[11,12] While experimental demonstrations on spin control and spin coupling of NV centers have been carried out in type IIa diamond, diamond nanocrystals are currently available only in the form of type Ib. For applications, such as the incorporation of these nanocrystals in solid state cavity QED systems, an important question is whether there still exist in these nanocrystals NV centers that can feature lifetime-limited spectral broadening with relatively small effects of spectral diffusion.

In this Brief Report, we report photoluminescence (PL) and photoluminescence excitation (PLE) studies of NV centers in type Ib diamond nanocrystals. For these studies, synthetic high-pressure high-temperature type Ib diamond microcrystals with an average size of 40 μm were irradiated by a 2 MeV electron beam with an average dosage of the order of 10^{17} electrons/cm^2 and were subsequently annealed in vacuum at 800 °C for 2 h. The irradiated and annealed microcrystals were then mechanically crushed to yield smaller nanocrystals. PLE spectroscopy of single NV centers in these nanocrystals shows that in spite of effects of spectral diffusion and spin-nonpreserving transitions that are common to NV centers in type Ib diamond, the zero-phonon linewidth as small as 16 MHz, approaching that of NV centers in high quality type IIa bulk diamond, can still be observed.

For PL and PLE studies, the diamond microcrystals and nanocrystals were dispersed on a silicon wafer. The sample was mounted on the cold finger of a liquid helium cryostat. Figure 1(a) shows the PL spectrum from a single diamond microcrystal obtained at 8 K. The sharp resonance at 637 nm with a spectral linewidth of 0.36 nm corresponds to the zero-phonon transition from the negatively charged NV (NV$^-$) centers. The broad emission at longer wavelength is due to phonon-assisted transitions, which are characteristic of defect centers in solids. Figure 1(b) shows the PL spectrum from a diamond nanocrystal obtained at 8 K. The inset of Fig. 1(b) also shows a scanning electron micrograph (SEM) of the nanocrystals.

The PL spectrum from the diamond nanocrystal shows multiple emission resonances with the linewidth of individual resonances narrower than that obtained from the microcrystal (the linewidth of the narrowest resonance is limited by the spectral resolution of the spectrometer system). Because of the abundance of substitutional nitrogen impurities in type Ib diamond, a single nanocrystal after irradiation and annealing contains a relatively large number of NV centers. The spectral distribution of these NV centers (~5 nm), however, is more than 1 order of magnitude broader than the PL linewidth of individual diamond microcrystals. Local strains induced by the mechanical crushing of the microcrystals lead to significant shifts in the transition frequency of the NV centers.

For PLE studies, the zero-phonon transition of the NV centers was excited resonantly. The estimated excitation laser focal spot size is 1 μm. Optical emissions arising from phonon-assisted transitions at wavelength longer than 650 nm were detected with a silicon photon-counting avalanche photodiode. Both holographic notch filter centered at 637 nm and red-pass filters were used to reject stray laser

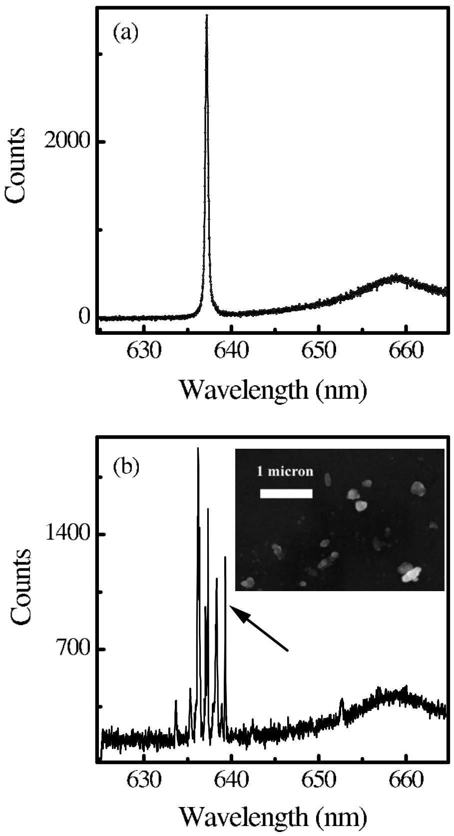

FIG. 1. (a) PL spectra obtained at 8 K from a single diamond microcrystal and (b) from a single diamond nanocrystal. The NV centers were excited with a laser beam at λ=532 nm. The inset of (b) shows a SEM image of the nanocrystals. The arrow in (b) indicates the NV resonance used for the photon correlation measurement in Fig. 4.

scattering as well as Raman scattering. Figure 2 shows repeated single scans of PLE obtained with a tunable diode laser (New Focus Velocity) from a nanocrystal. The frequency scan was performed by an external triangle ramp wave form. Each scan took approximately 2 s. In a single scan, the frequency shift varied from 40 to 0 GHz and then back to 40 GHz again. Accordingly, the two resonances shown in each scan of Fig. 2 correspond to emissions from the same NV center. No optical repumping was used during or between the scans. The NV center remained bright during the hundreds of repeated scans, although both the amplitude and spectral position of the NV emission fluctuated. Bleaching of the NV center was also observed after about 1 h of repeated scans. Since the occurrence of a spin-nonconserving transitions will set the NV center in a dark state, the PLE scans in Fig. 2 indicate that the particular NV center can undergo many cycles of spin-conserving transitions without incurring a spin-nonconserving transition. Note that the fluctuation in the spectral position observed in Fig. 2 is in part due to the drift in the diode laser frequency during the extended measurements.

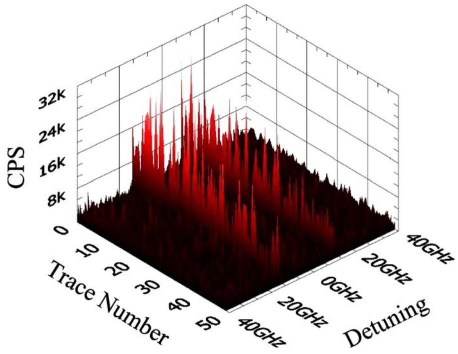

FIG. 2. (Color online) Repeated scans of PLE obtained at 10 K and with an excitation laser power of 200 nW. The zero-phonon peak occurs in both forward and backward scans at the same spectral position, and the two peaks correspond to emissions from the same NV center.

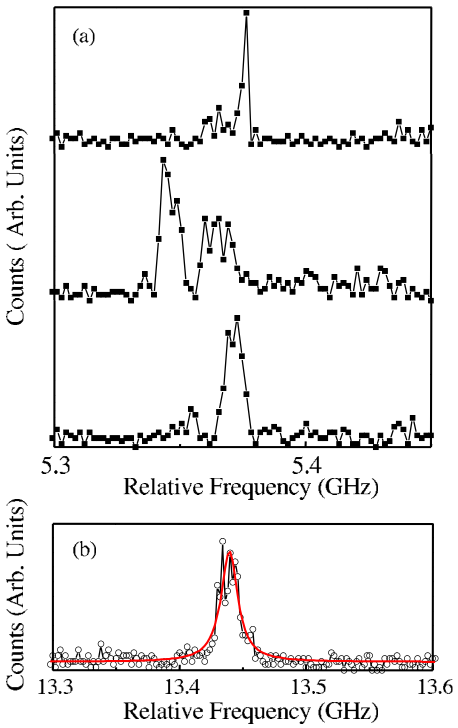

FIG. 3. (Color online) PLE spectra obtained at 10 K and with an excitation laser power of 300 nW. (a) Three representative PLE scans from a single NV center. (b) A single PLE scan from another NV center. The solid line shows a numerical fit to a Lorentzian line shape with a linewidth of 16 MHz.

For better spectral resolution, we have also carried out PLE studies by using a frequency-stabilized tunable dye laser (Coherent 899-21) with a linewidth of <1 MHz. Figure 3(a) shows three representative single PLE scans obtained at 10 K and from a NV center that featured relatively small effects of spectral diffusion during repeated scans. Again, no optical repumping was used during or between the repeated scans. The non-Lorentzian line shape of the PLE spectra in Fig. 3(a) indicates small spectral shifts of the NV transition frequency, while the laser was scanned across the zero-phonon resonance. While this NV center exhibits only a limited amount of spectral diffusion, the NV center spent significant amount of time in dark states (not shown). Note that as we have discussed earlier, local mechanical strains in diamond nanocrystals, indicated by the large inhomogeneous linewidth of zero-phonon NV emissions shown in Fig. 1(b) can alter the excited-state electronic energy structure of the NV centers. In addition, for a NV center in a particular nanocrystal, it is possible that after irradiation and annealing, large of fractions of nearby nitrogen atoms have formed NV centers, leading to relatively small effects of photoionization of nitrogen impurities.

Figure 3(b) shows a PLE scan from another NV center that features a Lorentzian-like line shape, indicating negligible effects of spectral diffusion when the laser was scanned across the zero-phonon transition. From the numerical fitting, we obtain a spectral linewidth (full width at half maximum) of 16 MHz, approaching the narrowest and lifetime-limited homogeneous linewidth obtained for NV centers reported for high purity type IIa diamond.[12] This NV center, however, showed relatively large spectral shifts after repeated PLE scans.

In addition to PL and PLE studies, we have also used photon correlation to characterize the behavior of single NV centers. Since typical nanocrystals contain a large number of NV centers, resonant excitation was used for the photon correlation measurement. Figure 4 shows the result of the photon correlation measurement for the NV resonance, as indicated by an arrow in Fig. 1(b). The normalized photon correlation falls below 0.5, confirming that the resonant excitation excites primarily a single NV center.[13,14] Note that at relatively high excitation levels, no Rabi oscillations were observed in the photon correlation. The NV transition frequency is not stable during the extended time period needed for the correlation measurements. The frequency fluctuation leads to corresponding fluctuations in the generalized Rabi frequency, preventing the observation of Rabi oscillations in the photon correlation.

It should be pointed out that statistically, only a very small fraction of NV centers in our PLE measurements remain bright or exhibit only small effects of spectral diffusion during repeated PLE scans. An overwhelming majority of the NV centers in diamond nanocrystals features strong effects of spectral diffusion and spends a significant amount of time in dark or optically inactive states. For these NV centers, it becomes difficult to track the behavior of individual NV centers.

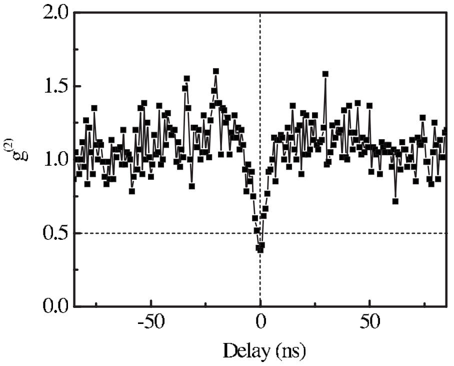

FIG. 4. Photon correlation measurement obtained at 10 K. The NV center is resonantly excited with an excitation power of 100 nW.

In summary, we show that nearly lifetime-limited zero-phonon linewidth can be observed for NV centers in diamond nanocrystals, although given the abundance of nitrogen impurities present in type Ib diamond, most NV centers also feature strong effects of spectral diffusion. These results further suggest that for the use of NV centers in applications such as cavity QED, where effects of spectral diffusion are detrimental, it might be highly beneficial to preselect diamond nanocrystals with desired characteristics before their incorporation into a cavity QED system.[15]

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