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I. THE NITROGEN VACANCY CENTER

The nitrogen vacancy (NV) color center in diamond is a point-defect consisting of a substitutional nitrogen atom adjacent to a vacant lattice site. In general, NV centers can occur in either a neutral (NV^0) or negatively charged (NV^-) electronic state. In the following, we will restrict our discussion to case of NV^- [1]. The ground state of the NV^- is a spin triplet with the $|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$ spin projections split by a zero-field splitting, $\Delta = (2\pi) \times 2.8$ GHz, owing to spin-spin interactions [2, 3]. The $|m_s = \pm 1\rangle$ states can further be Zeeman-split by applying an external magnetic field. The coherent manipulation of all electronic spin states can be achieved via microwave irradiation. For diamond samples with a low concentration of paramagnetic impurities, the coherence times of the electronic spin are typically a few milli-seconds [4].

The electronic ground state and the first NV^- excited state both lie within the band gap of diamond. The transition between these two states is dipole allowed and can be excited under green illumination, with subsequent emission between 637 nm and 800 nm [2, 3]. While optical excitation from the $|m_s = 0\rangle$ state is spin preserving, excitation from $|m_s = \pm 1\rangle$ has a finite branching ratio into a metastable singlet with a lifetime of 300 ns. This singlet state decays non-radiatively into $|m_s = 0\rangle$ allowing for an efficient initialization of the electronic spin. The long lifetime of the singlet state also enables optical read out of the spin state since the $|m_s = \pm 1\rangle$ states will appear darker [2, 3].

II. MATERIALS AND METHODS

Optical Setup

The optical setup consists of a home-built confocal microscope with two independent scanning beams. Two separate green excitation/collection beams are used for simultaneous excitation of spatially separated nanoparticles [5]. One of the scanning beams is controlled by a galvo-scanner

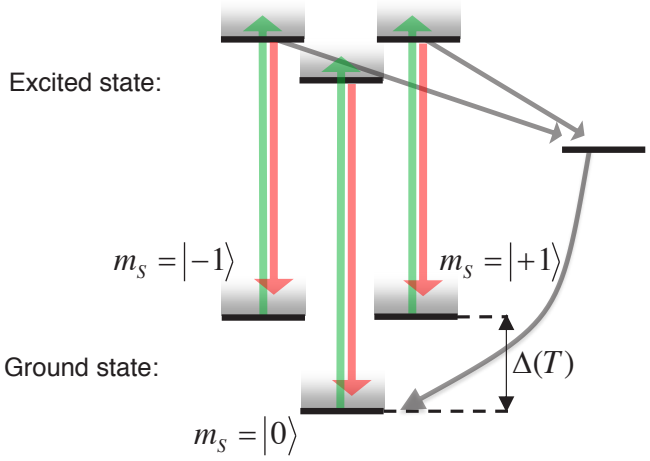

FIG. S1: **— NV Level Scheme.** Simplified level scheme for NV^- defect. Green arrows indicate optical excitation via a 532 nm laser. Red arrows represent spin conserving fluorescence, while the grey arrows depict (non-radiative) shelving into the metastable singlet state as well as decay back down to $|m_s = 0\rangle$.

(Thorlabs GVC002); the other beam is controlled by a 3-axis piezoelectric stage (PI P-562.3CD). The collected light is transmitted through a dichroic mirror and filters before being focused onto an avalanche photo diode (APD). The samples measured in Fig. 3 and 4 of the main text are mounted on a microscope coverslip; in the case of biological samples, the cells are protected by a buffer solution housed in a PDMS ring (Fig. S2).

Nanoparticle Localization

Under green excitation, the gold nanoparticles (Au NPs) used in the present work exhibit an emission spectrum which is slightly blue shifted relative to the NV spectrum (Fig. S3). This allows us to use a frequency doubled YAG laser (532 nm) for excitation of both NV centers and Au NP. To distinguish the fluorescence of nanoparticles from NV centers, a 560 ± 25 nm band pass filter is used. By comparing scans with and without a band pass filter (Fig. S4), it is possible to clearly identify the location of Au NPs. To verify the presence of a nanodiamond (ND), we utilize the electron spin resonance (ESR) response of NV centers; in particular, we measure changes to the photoluminescence under microwave excitation.

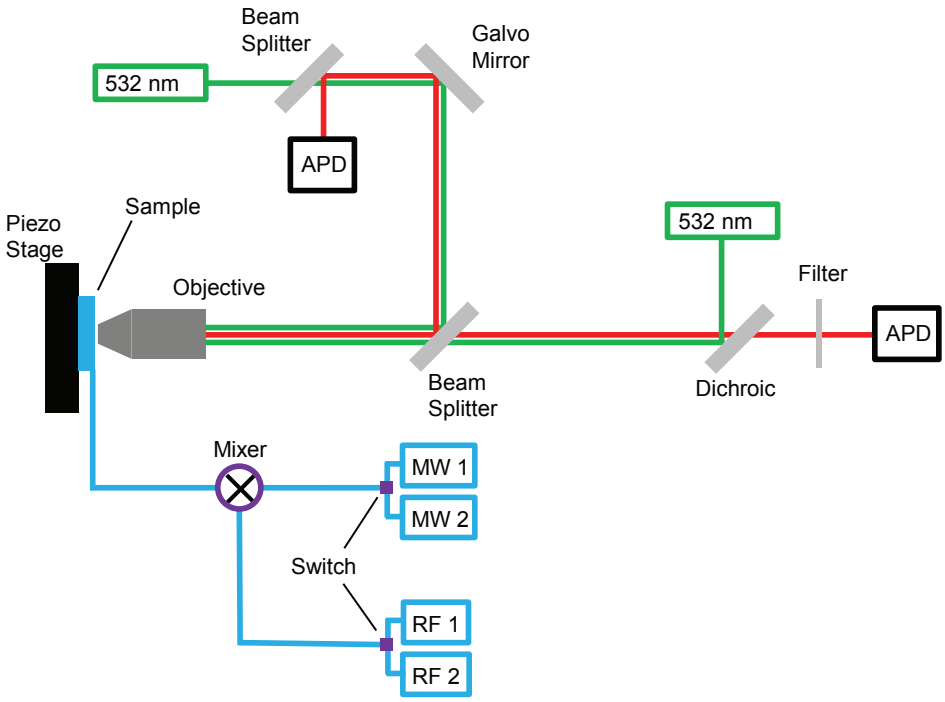

FIG. S2: **— Schematic Setup.** Depicts the optical (excitation: green, collection: red) path and microwave supply (blue). Each of the two excitation (collection) paths can be independently controlled using a combination of a galvo-mirror and a piezo. By controlling the MW switches, it is possible to interchange between four different MW frequencies on sub-microsecond time scale.

Microwave Setup

The microwave excitation of NV centers is achieved via a coplanar waveguide that is lithographically fabricated on top of the microscope coverslip. In the experiments shown in Fig. 3 and 4 of the main text, CW microwave pulses at four different frequencies are applied in order to probe the fluorescence rate at different microwave frequencies. These microwave frequencies are created by mixing low frequency RF fields (200 and 202 MHz) with two different microwave carrier frequencies around 2.68 GHz. The actual pulse sequence is illustrated in Fig. S5. To eliminate sensitivity to low frequency noise in the ND's photoluminescence, the pulse sequence depicted in Fig. S5 is repeated at a 5 kHz sampling rate.

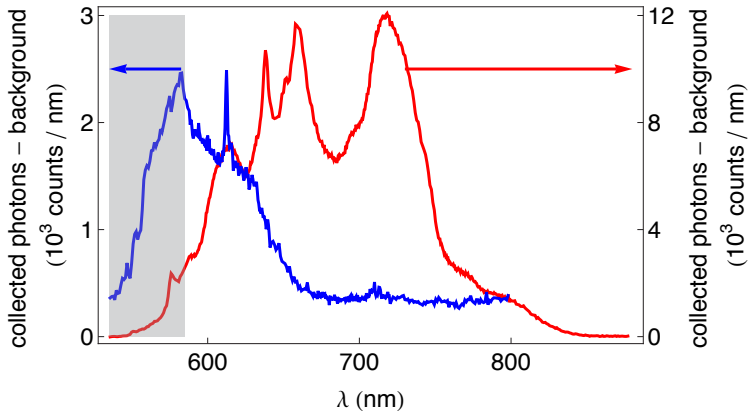

FIG. S3: **— Fluorescence spectrum** under green excitation of gold nanoparticles (blue data) and nanodiamonds (red data). The shaded region indicates the bandpass filter used for detection of gold. The arrows mark the respective y-axis scaling for each curve.

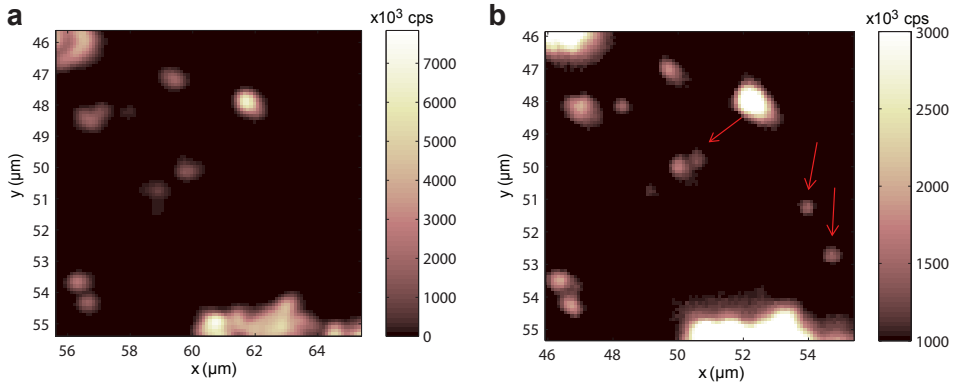

FIG. S4: **— Confocal image of nanoparticles. (a)** Confocal scan of Au NPs and NDs taken with a 633 nm longpass filter. **(b)** Scan of the same area using a 560 ± 25 nm bandpass filter. For visual clarity, a lower bound of 1000 kcps and an upper limit of 3000 kcps is set. The red arrows indicate locations of Au NPs.

Global Temperature Control

To achieve a homogenous heating of the sample in our validation/calibration experiments, the sample mount is fabricated out of solid copper and is thermally isolated from the rest of the experiment. A Peltier element is attached to the sample mount in order to control the temperature. The data in Fig. 2 of the main text are obtained by heating the sample mount (by 1K) and then subsequently cooling down after switching off the Peltier element. Thermal equilibrium is reached

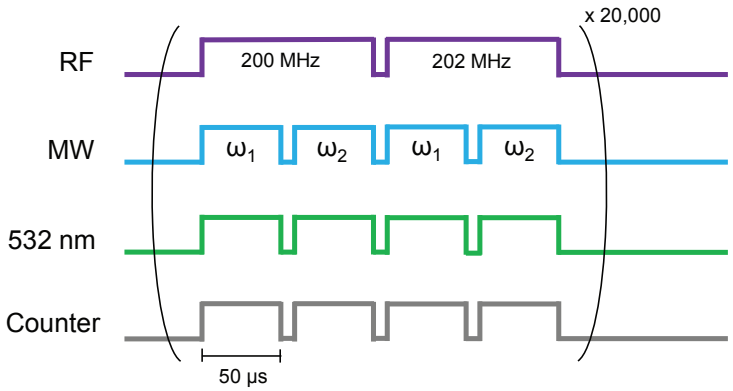

FIG. S5: **— Pulse sequence** used for the measurements of Fig. 3 and 4 of the maintext. The microwave (MW) frequencies ω_1 and ω_2 are chosen such that when mixed with 200 MHz and 202 MHz fields, four frequencies $f^1 = \omega_1 + 200$ MHz, $f^2 = \omega_1 + 202$ MHz, $f^3 = \omega_2 + 200$ MHz and $f^4 = \omega_2 + 202$ MHz around 2.87GHz are realized. Each pulse is 50 μs long and the entire sequence is repeated $20,000$ times.

after approximately 1 hour. During the process of this equilibration, the measurement shown in Fig. 2 of the main text was recorded. The sample temperature (x-axis of Fig. 2) is independently recorded by a thermistor located on the sample mount immediately next to the diamond. The data shown in the inset in Fig. 3c is obtained by using a similar mount. Each data point is taken by first stabilizing the temperature of the mount through an attached Peltier element. After stabilization, the shift of the NV zero-field splitting is measured.

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