Antibunching Analysis and Confocal and Atomic Force Microscopy of Room Temperature Single-Photon Sources

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In this paper, photon antibunching results are discussed for nitrogen-vacancy nanodiamonds in a cholesteric liquid crystal host and cadmium selenium telluride quantum dot single emitters both in a colloidal solution and fluorescence enhanced by a plasmonic bowtie antenna. Results were obtained using a Hanbury-Brown and Twiss interferometer in combination with a confocal microscope. Further analysis was made on nanodiamond samples using an atomic force microscope. Only the quantum dots showed any signs of antibunching, although with seemingly increased efficiency while within the nanoantenna. Further analysis must be done to investigate why the nanodiamonds did not show antibunching.

*Keywords*: Antibunching, single photon sources, quantum dots, nanodiamonds, single-emitters, plasmonic nanoantenna.

I. Introduction and Theory

In order to realize ambitious applications of quantum optics in the information industry, such as quantum cryptography, computing, and teleportation, it is critical to develop widely available and reliable single-photon sources. Beforehand though, it must also be ensured that the source used is truly a single-photon source, and antibunching must be observed. This report will describe the experiments and results of testing different room temperature single photon sources for antibunching, as well as additional attempts at characterization of the sources such as atomic force microscopy.

*Room Temperature Single Photon Sources*

In an ideal situation, the single photon sources used for quantum optics based communication should be stable at room temperature. The most viable candidates (or single-emitters) for this are fluorescent dye molecules, nanocrystals, and quantum dots.\(^1\)

When one of the molecules in these single-emitters is hit by a photon with sufficient energy, an electron in a lower energy level of the molecule is excited to a higher orbital. After a certain average time known as the fluorescence lifetime \(\tau_F\), the electron will come back down to its ground state level and in the process emit a fluorescent photon. Further, the typical fluorescence lifetime can be on the order of 0.5 to 20 ns. Consequently, since the time intervals between fluorescent emissions are approximately discrete, the emitter can potentially be used as a true single-photon source.\(^1\)
One way of increasing the efficiency or quality of fluorescence is the use of photonic bandgap materials which are then doped with single-emitters. Photonic bandgap materials are periodic structures that are able to reflect a specific range of wavelengths of light. Further, there are certain bandgap materials which can also be made to have polarization selectivity, an example being a cholesteric liquid crystal (CLC) host. These liquid crystals are chiral and nematic, meaning the mirror image of the molecules making up the crystal cannot be superimposed, and that they are only approximately aligned in a certain direction. As a result, the liquid crystals arrange themselves to have a certain handedness about an axis, which makes it so that only light with the same handedness circular polarization can experience the bandgap.\(^2\)

It is possible to control the central wavelength and bandwith of the CLC bandgap by changing the pitch (twice the period of the structure) and extraordinary and ordinary refractive indices \((P, n_e, n_o)\), respectively. The central wavelength \(\lambda_0\) can be calculated using the formula

\[
\lambda_0 = P \frac{n_e + n_o}{2}.
\]

and the bandwith \(\Delta\lambda\) can be calculated using

\[
\Delta\lambda = 2\lambda_0 \frac{n_e - n_o}{n_e + n_o}.
\]

Moreover, the CLC can be engineered to improve the efficiency of the single photon source by matching the bandgap edge to be right at the wavelength of maximum fluorescence in the emitter.\(^7\) It is also very interesting that using different combinations and ratios of liquid crystal molecules, the output polarization and central wavelength are easily customizable.\(^3\)

**The Second Order Coherence Function and Antibunching**

There are three different kinds of single photon sources, characterized by the Poissonian statistics which most accurately describe the photons emitted (Figure 1). Bunched single photon sources, such as a lamp emitting thermal light, are those in which photons are regularly emitted close to one another in time. In a random (or coherent) light source, such as a laser, photons are still emitted as bunches in time, but the spacing is more random than and not as bunched as in thermal light. Finally, in antibunched single photon sources, photons are emitted at regular intervals that are more equally spaced and less bunched than in a random source. In essence, antibunched light offers a greater probability of detecting two photons at different times than detecting them at different places.

Formally, the metric used to deem a single photon source as bunched, random, or antibunched is the normalized second order coherence function

\[
g^{(2)}(r_1, t_1, r_2, t_2) = \frac{\langle I(r_1, t_1)I(r_2, t_2) \rangle}{\langle I(r_1, t_1) \rangle \langle I(r_2, t_2) \rangle},
\]

where \(I\) is the intensity and \(r\) and \(t\) are the distances from the source to the detector in both time and space, respectively, subscripted for two separate detectors.\(^3\) However, in the experiments
which are described in this report, a Hanbury-Brown and Twiss interferometer setup was used, where the distances from two detectors are made equivalent by a beam splitter. As a result, \( r_1 = r_2 \), and it is only the time difference \( \tau \) between detections at both detectors that is essential. Thus, \( g^{(2)} \) reduces to the expression

\[
g^{(2)}_{T,R}(\tau) = \frac{\langle I_T(t+\tau)I_R(t) \rangle}{\langle I_T(t+\tau) \rangle \langle I_R(t) \rangle},
\]  

where the subscripts \( T \) and \( R \) denote, respectively, the transmitted and reflected light after the beam splitter.\(^1\)

In the case that only the measurements that occur simultaneously are analyzed (\( \tau = 0 \)) and a 50/50 beam splitter is used, then by manipulating the classical relations between transmission and reflection coefficients \( g^{(2)} \) reduces even further to

\[
g^{(2)}_{I,I}(0) = \frac{\langle I_I(t) \rangle^2}{\langle I_I(t) \rangle^2}. \tag{5}
\]

Finally due to the Cauchy-Schwartz inequality, the last result shows that, for classical light

\[
g^{(2)}_{T,R}(0) = g^{(2)}(0) \geq 1. \tag{6}
\]

Thus, in order to deem a single photon source as antibunched, then this inequality must be violated, and \( g^{(2)}(0) \) must be found to be less than 1.\(^1\)

\[\text{Figure 1. Second Order Coherence Function Plots for Bunched, Random, and Antibunched Sources. Red: bunched; green: coherent; yellow: antibunched.}\]

However, since the number of photons incident on a detector is proportional to the intensity, then it is possible to use photon counts in order to calculate or estimate the value of \( g^{(2)}(0) \). And to estimate the value, the plots of photon counts versus interphoton times can be compared to the idealized \( g^{(2)}(\tau) \) plot for antibunched light (Figure 1). When plots of counts versus time have a downwards cusp shape, it is known that antibunching has been achieved.\(^1\)
II. Experimental Setups and Descriptions

A. Confocal Microscopy and Antibunching Verification

The two primary instruments used for measuring antibunching were the confocal microscope (CM) and the Hanbury-Brown and Twiss interferometer (HBTI). With the latter, it is possible to image samples through a raster scan, and with the former a single point on the sample can be analyzed in order to verify antibunching.

![Diagram for Confocal Microscopy and Photon Antibunching Experiments](image)

**Figure 2.** Diagram for Confocal Microscopy and Photon Antibunching Experiments. Green light: 532nm; yellow: 579 nm fluorescence (CdSe quantum dots). Top-left inset shows oil immersion microscope objective. The beam is first cleaned up and attenuated to single photon level. After the dichroic mirror, the fluorescence is imaged by x-y raster scanning a sample and measuring the photon counts at each point using either of two avalanche photodiodes in a Hanbury-Brown and Twiss interferometer setup. The first beam splitter the fluorescent light encounters gives the user the option of wide-field (WFM) imaging of focused and un-focused light with an electron-multiplying CCD camera or the microscope’s eyepiece. The second (50/50) beam splitter is crucial for determination of antibunching.

In most antibunching experiments that were carried out, the light source used to excite fluorescence in the samples was a 6 ps pulsed laser with a wavelength $\lambda_0$ of 532 nm, frequency doubled through second harmonic generation from 1064 nm within a laser diode module (Figure 2). Further, since the light coming directly from the laser did not have a pure spectrum and was elliptically polarized, an interference filter was placed directly in front of the laser in order to only...
pass light at $\lambda_0$ and correct the circular polarization. Following the blue filter, the beam was then cleaned up and expanded using a spatial filter consisting of a microscope objective, lens and a pinhole. Additionally, there were four mirrors placed throughout in order to facilitate alignment and direct the beam towards the CM. However, right before entering the CM, several neutral density (ND) filters were placed in order to attenuate the laser beam.

Once the photons entered the CM frame, a removable dichroic mirror reflected the $\lambda_0$ photons towards a 1.35 numerical aperture ($NA$) microscope objective that focused the beam onto the sample. Crucially, the objective was immersed in oil and set against the sample, allowing for a greater solid angle of the fluorescent photons to refract back towards the microscope objective and towards the other parts of the CM and HBTI. Although some of the $\lambda_0$ light reflected back as well, the dichroic mirror would not let any of it pass through further. However, for assurance, a removable orange interference filter was placed right after the dichroic mirror in order to eliminate any remaining $\lambda_0$ photons.

Next, the fluorescent photons encountered a non-polarizing beam splitter (NPBS), which provided the option of sending the beam to either an electron-multiplying CCD (EMCCD) camera for alignment or towards the HBTI. Using either port, part of the light also goes towards a mirror which leads to more relay optics and the eyepiece. Additionally, when looking at the sample through either the eyepiece or the EMCCD camera, it was necessary to remove both the dichroic mirror and the orange filter in order to have additional $\lambda_0$ light for easily resolving an image.

In essence, the CM system has the same resolution that a WFM would have with the same optics. The diffraction limit or spot size radius $\Delta x$ of the CM resolution could be calculated using the Rayleigh criterion

$$\Delta x = \frac{1.22 \lambda}{NA},$$

where $\lambda$ and $NA$ are the wavelength and numerical aperture, respectively. The laser wavelength used to excite fluorescence in the samples was 532 nm, frequency doubled through SHG from 1064 nm within the laser source, and the $NA$ of the microscope objective used was 1.35. Using (7), the limiting spot size radius is 0.481 microns. However, what makes the CM superior over a WFM is the greatly enhanced contrast due to spatial filtering of scattered light from areas of the sample which are not focused on.

After alignment, the CM port was changed in order to direct the light towards a focusing lens and the 50/50 beam splitter in the HBTI. It was then possible to raster scan an image which was relayed via additional electronics towards the computer display screen. For this, a LabView program (VI) was used to control the range or size of the raster scan on the sample, the step size, and the exposure time. Within the set exposure time, the two avalanche photodiode (APD) modules in separate arms of the HBTI acquired a count of the number of photons from each point of the sample, so two separate but similar images were produced. Further, no extra pinholes were placed in the system to work as the “confocal” part of the CM, since the apertures of the APD modules were sufficiently small to function similarly. At this point, and if necessary, the ND filters were changed in order to increase or decrease the brightness of the images displayed on the VI.
If a point on the completed raster scan was selected at the location of a single emitter, then the HBTI was used for its purpose of verifying antibunching. The reason two APDs were used was to compensate for the dead time, or the time interval in which the detection system lags after an individual photon is detected. Using the intensity correlation measurements from both APDs, it was possible to reduce the uncertainty created by the dead time.\(^1\)

**B. Atomic Force Microscopy**

For the nanodiamonds used to verify antibunching, an atomic force microscope (AFM) was also utilized to measure the surface topology of the sample.

**Figure 3.** Diagram of Atomic Force Microscope Working Principle. Not to scale. The laser is focused onto the cantilever end to which the scanning tip is attached, and the reflections from the cantilever are relayed to a position sensitive photodetector. The data acquired from the latter allows for recording changes in altitude as the sample stage moves and the tip is dragged across the sample. Further, in contact mode, a feedback loop ensures that the cantilever stays at a constant position, either by moving the stage or using the piezoactuator. In non-contact mode, the cantilever is oscillated near its resonance frequency by the piezoactuator.
The basic principle of AFM lies within the tiny cantilever and nanoscale tip used to scan the sample which is placed on a piezoelectric translation stage (Figure 3). Small amounts of voltage are applied to parts of the stage in order to move it in the x-y plane while holding the cantilever either stationary (contact mode) or constantly oscillating near its resonance frequency (tapping mode). In both operating modes, a laser source is focused onto the end of the cantilever to which a tip with radius of a few nanometers is attached.\(^4\)

As the tip probes the sample, it encounters changes in height due to interactions with Van Der Waals, dipole-dipole, and electrostatic forces, which makes the cantilever change altitude as well. This causes the focused laser to reflect at different angles, and these changes are relayed either directly or by a mirror to a position sensitive photodetector. Consequently, in order to maintain the stability of contact or tapping mode, the photodetector sends a signal to the feedback loop, which signals the vertical piezoactuator either in the stage or attached to the cantilever to change height. Moreover, this voltage control and feedback loop is crucial in avoiding excessive damage to the tip.\(^4\)

As for the modes, contact is mostly useful for topology measurements in solid samples, and tapping is more adequate for biological or moist samples. This is due to the possibility of the sample developing a thin layer of moisture on top, to which the tip could become stuck if the AFM is operated in contact mode. In tapping mode, only changes in the amplitude of the cantilever’s oscillation are sensed by the electronics due to the same forces mentioned above, and the feedback loop also controls the oscillation to maintain the amplitude constant.\(^5\)

However, there is a slightly different operational mode referred to as non-contact. Unlike in tapping mode where the tip still intermittently comes in close contact with the surface, the tip maximally hovers at ~10 nm above the sample surface. The main difference is that at this separation distance, the tip will only experience attractive Van Der Waals forces. Further, since non-contact mode leaves the least amount of damage on both the tip and sample, it is usually preferred over the other two.\(^6\)

Overall, atomic force microscopy offers the advantage that it can be regularly carried out at room temperature and in ambient settings, and provides resolution that is only limited by the radius of the tip. In vacuum conditions, it is even possible to image single atoms if they are arranged in periodic lattices. The main disadvantages however are that, for example, unlike scanning electron microscopy, the scanning time required for a sample is very large, and usually the sample size is limited to several square microns in size as opposed to square millimeters. Still, it is a very useful technique in the characterization of single-emitter surface topology by offering a three dimensional view of samples.
III. Sample Preparation Procedures and Results

Fluorescence phenomena were analyzed in three kinds of single emitters—nitrogen-vacancy nanodiamonds, cadmium selenium telluride (CdSeTe) colloidal quantum dots, and CdSeTe quantum dots placed at the center of a gold bowtie nanoantenna. In addition to this, a nanodiamond doped with photonic band gap materials (cholesteric liquid crystals) was also examined. Further details on these single emitters and photonic band gap materials are discussed below.

A. CdSeTe Quantum Dots

Quantum dots are actually semiconductor nanocrystals. Quantum dots show the property of fluorescing at different wavelengths with different size. Many quantum dots must be operated at cryogenic temperatures, but there are several types that had shown fluorescence at room temperatures\(^7\), making them a promising source of single photons much like NV-nanodiamond. In this experiment CdSeTe quantum dots are employed as single emitters.

When preparing the CdSeTe colloidal quantum dots, we used a pipette to drop a small amount of a low concentration solvent onto a glass slide. The slide was then coated by spinning at a high rotation speed, by which the quantum dots are uniformly spread.

![Figure 4.](image) (Left) Micrometer confocal raster scan of CdSeTe quantum dots; 3 and 3.5 order of magnitude optical density filters and a 0.45 mW HeNe laser source were used. (Right) Image of quantum dots viewed under the EM-CCD camera.

By employing the confocal microscope, the fluorescence of quantum dots was captured. As we can see in Figure. 1(left), several spots have tiny lines over the quantum dots, which were caused by blinking when scanning apparatus was at a translation stage. Although quantum dots can absorb and emit photons, the dots do not fluorescence continuously. Thus, the delay between absorption and emission is called blinking. The stripes we saw on figure 1 were because that the microscope scanned the place where quantum dots were blinking, which caused the shift in measured intensity.

Also, The EM-CCD camera was used to image the quantum dots, as can be seen in Figure 1(right). We also used the camera view to coarsely focus the system before performing raster scans of the individual quantum dots. Compared to confocal microscope, there was no pinhole, which helps to observe a wide field view of the quantum dots emitting photons.
Figure 5. Signal Intensity versus Time While Scanning. The sample showed an obvious blinking phenomenon. This corresponds to the confocal microscopy raster scan in Figure 4.

Figure 6. Histogram Corresponding To Quantum Dot Indicated By Green Cross in the Confocal Raster Image in Figure n. The dip at ~40 ns indicates fluorescence antibunching.

After achieving the fluorescence image under the confocal microscope, we can direct a focused beam on an individual quantum dot. By exciting just one quantum dot, the emitted fluorescence will be characterized as antibunched light. A Hanbury Brown and Twiss setup along with a Time Harp computer card records the time between photons incident on a pair of avalanche photodiodes (APD a and APD b). This data is represented as a histogram of counts versus time delay between photons. We took 13 quantum dots for measurement and found the eight to be the best one, which established the most obvious anti bunching behavior and had the most obvious dip (Figure 6).

B. Nitrogen Vacancy Nanodiamonds

NV nanodiamonds are nanocrystals with color centers. The color centers occur when a lattice vacancy becomes trapped next to a nitrogen impurity in diamonds. Vacancies can be created through electron irradiation at energies greater than 200 keV.\(^8\)
The sample we prepared for the confocal microscope was made by using the nanodiamonds to dope a cholesteric liquid crystal (CLC). We used a capillary tube to apply the liquid crystal and nanodiamond solution to a glass substrate. The capillary tube was used to mix the solution, and once the solution was adequately mixed, a cover slip was applied on the substrate. We wait until the solution form a uniform film and then use it as a sample to observe.

![Figure 7](image1.png)

**Figure 7.** (Left): Micrometer confocal raster scan of NV-nanodiamonds. (Right): Image of NV-nanodiamonds viewed under the EM-CCD camera

We also used the confocal microscope combined with the Hanbury-Brown and Twiss interferometer and TimeHarp 200 computer card and software. We tested several points of the nanodiamond sample, and their counts with respect to interphoton times were observed and plotted. We could not see an obvious dip in the curve, so there was no obvious antibuching after testing 11 spots; the typical histogram is shown in Figure 8. The reason that no antibunching was observed may lie in the fact that the nanodiamonds are clustered. On the other hand, this showed just how difficult it would be to achieve antibunching.

![Figure 8](image2.png)

**Figure 8.** Histogram of Antibunching Measurement for Nanodiamonds. No antibunching was visible.
After fluorescence imaging, we investigated the surface topology of the nanodiamond sample by using the atomic force microscope (AFM). The samples were prepared using a 10μL nanodiamond solution diluted by a factor of 2000, and the topology measurements are shown in Figure 9. The image showed stripes and shadows due inherent flaws (i.e. hysteresis, creep, nonlinearity) associated with atomic force microscopy, which can be considered as background noise for larger scans and flaws in the tip for smaller scans. Although the size of nanodiamonds in this sample is typical, we cannot say that there are not so many clustered nanodiamonds. Thus, more research should be done to investigate the reason why we cannot see antibunching in our sample. Whether it's because of clustering remains unclear.

![Figure 9. Atomic Force Microscopy Images of Nanodiamonds. (Left): an overall image of the nanodiamonds. (Right): Image of one typical nanodiamond; its dimensions are about 100 nm by 100 nm.](image)

Lastly, the EM-CCD Camera along with a diffraction grating spectrometer was also used to attempt to image the spectrum of the nanodiamonds' fluorescence. The graph below (Figure 10) shows the spectrum of the calibration source, with sharp peaks at 99.1 nm, 273.5 nm and 322.1 nm. These peaks did not correspond to the correct wavelengths in the calibration source, so no further experimentation was done with this. The spectrum captured both by the CCD camera and the spectrometer are also overlapped, and we can see that the peaks and the spectrum are highly correlated.

![Figure 10. The spectrum of the spectrometer calibration source obtained using the EM-CCD camera along with a diffraction grating spectrometer. The spectrum obtained by CCD camera and the spectrometer are overlapped.](image)
C. CdSeTe Quantum Dots in a Plasmonic Bowtie Nanoantenna Cavity

The last emitters we checked in this lab were CdSeTe quantum dots placed in the middle of a gold bowtie nanoantenna. We did not prepare the gold bowtie, which is usually fabricated by lithography. Figure 11 (left) shows a scanning electron microscope image of the gold bowtie prepared by S. Lukishova; there is a 50 nm gap in the center. The image (of the gold bowtie nanoantenna) which we acquired using the confocal microscope is shown in Figure 11 (right); the numbers in the image are used as a reference.

![Figure 11](image.png)

Figure 11. (Left): Scanning electron microscope image of a gold plasmonic bowtie nanoantenna prepared by S. Lukishova. (Right): The image of a gold bowtie nanoantenna we obtained through confocal microscopy.

![Figure 12](image.png)

Figure 12. (Left): Confocal microscope raster scan of CdSeTe quantum dots at the center of a gold bowtie nanoantenna. (Right): Signal intensity versus time while scanning. The CdSeTe quantum dots showed an obvious blinking phenomenon.

We also used the confocal microscope to see the fluorescence of the CdSeTe quantum dots in the gold bowtie cavity, and the image obtained is shown in Figure n. Also, the signal intensity changing with time is plotted in Figure n, from which we can see obvious blinking behavior.

The next investigation we did on the quantum dots was antibuching. We first measured the zero delay of the system, as shown in Figure n. A signal from one APD was split and sent to both ports of the Timeharp 200 computer card. This created two TTL (transistor-transistor logic) pulses
which represent a simultaneous arrival. In reality there is a delay between the arrival at the two ports, and this delay is presented in Figure n. This particular time is the zero time, and when an antibunched histogram is collected there should be a dip at the zero time. If two photons are bunched together, then the beam splitter could send them to separate APDs, thus being binned at the zero time. This should not happen with antibunched light.

![Figure 13. Histogram of the zero delay of the laser system.](image)

After that, the laser beam was focused on the green cross area in Figure 8 (left) and the histogram was constructed through the Time Harp software, as shown in Figure n. The histogram displayed obvious cusps, which indicated good antibunching.

![Figure 14. Histogram constructed via the Time Harp program of CdSeTe quantum dots placed at the center of a gold bowtie nanoantenna.](image)
IV. Conclusion

Antibunching behaviors of single emitters such as NV-nanodiamonds, colloidal CdSeTe quantum dots, and CdSeTe quantum dots in a plasmonic bowtie nanoantenna were investigated in this paper. Confocal fluorescence microscopy was used to image the samples and to focus on single-emitters. Antibunching behavior was investigated by plotting the histogram of photons arriving at different time intervals captured by the Time Harp 200 computer card. Several sets of data we obtained did not show obvious antibunching. The reason may be that the sample exhibited clustering, which remains to be proven. The AFM images we acquired did not show strong evidence of clustering. Overall though, we obtained good antibunching in both samples of quantum dots, and obvious blinking behavior of these particles was observed.

V. Acknowledgements

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Note
Yiming: III, IV, V

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