

Fluorescent Nanodiamonds

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Recently, fluorescent nanodiamonds (NDs) have garnered much attention for their potential use as fluorescent tags in biological systems, as well as for the sensing applications made possible by the unique spin properties of the nitrogen-vacancy fluorescent defect. Diamonds are an allotrope of carbon admired for their beauty, exceptional hardness, and durability. These properties are the result of the molecular structure of diamond, which is composed of carbon atoms bound tetrahedrally to each other, resulting in a lattice with face-centered cubic symmetry. This structure gives diamonds a high refractive index and high density relative to other carbon allotropes. While diamonds are not the thermodynamically favored allotrope under standard conditions, they can be formed in conditions of high temperature and high pressure.¹

The smallest possible diamonds are the diamondoids, such as adamantane, which are naturally present in crude oil. Larger NDs (up to ~100 nm) are prepared by a variety of methods. High pressure high temperature synthesis (typical conditions are around 1400 °C and 5-6 GPa) is the predominant industrial method for synthetic diamond production. Chemical vapor deposition is another common method of diamond synthesis. These methods usually produce micron-sized diamonds or larger, which can be milled to produce NDs. NDs can also be produced through the detonation of explosives in sealed containers. Detonation NDs tend to be 4-5 nm in diameter.¹

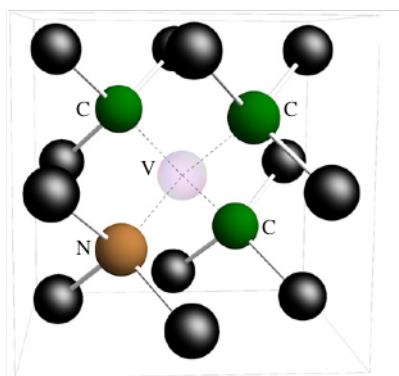


Figure 1: A diagram of the NV⁻ defect in the diamond

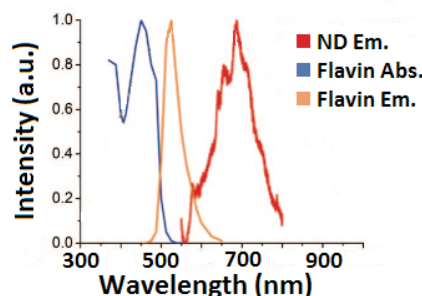


Figure 2: Comparison of the emission and absorption

Pure diamonds are naturally colorless, and color in diamonds results from chemical impurities or lattice defects. The predominant impurity in natural diamonds is nitrogen, which gives diamonds a yellow to brown color. Irradiation of diamonds by high energy particles can produce lattice vacancies, which appear as a green color in bulk diamonds.² In diamonds with atomically dispersed nitrogen impurities, irradiation and subsequent annealing above 600 °C creates defects that fluoresce at 638 nm, now known to be nitrogen-vacancy (NV) pair defects. The NV defect was first observed by du Preez

in 1965, who hypothesized that a nitrogen-vacancy pair had been formed based on the synthetic process.³ Davies and Hamer later determined the defect center must have trigonal symmetry (the C_{3v} point group) with its rotational axis in the $\langle 111 \rangle$ direction.⁴ An EPR study of the defect by Loubser and Van Wyk revealed that the NV defect has an $S=1$ spin state, which agreed with previous symmetry models if it was assumed the defect was negatively charged with six electrons (NV^-).⁵ The defect arrangement is shown in Figure 1.

The potential use of NDs as biomarkers was first recognized by Chang et al. in 2005.⁶ In their initial study, they noted that the NV^- defect of 100 nm fluorescent NDs is photostable even after 8 hours of illumination under a mercury lamp and possesses an absorption cross-section at 560 nm of $5 \times 10^{-17} \text{ cm}^2$, similar to that of conventional organic dyes.⁶ In another study, the researchers compared the emission of 35 nm NDs to a representative flavin molecule, showing that the absorption and emission maxima of the NV^- defect do not coincide with cellular autofluorescence (400-550 nm), as shown in Figure 2.⁷ The researchers were also able to modify the ND surface with poly-L-lysine through the formation of amide bonds with ND surface carboxyl groups, showing the possibility of functionalizing NDs without affecting fluorescence. Currently, analysis of ND surface functionalization is only qualitative.¹

Comparing fluorescent NDs to quantum dots, a typical quantum dot may have an absorption cross section around 10^{-15} cm^2 , and both particle types have a quantum yield of about 0.8, and thus a quantum dot is brighter than a single defect in a ND.⁸ A ND, however, may contain multiple fluorescent defect centers. In the Study by Chang et al.⁷, one 35 nm was about as bright as a CdSe/ZnS quantum dot emitting at the same wavelength. Fluorescent NDs generally show greater photostability than quantum dots, but quantum dots are much smaller, with a maximum size of 10 nm including the passivation layer. In current fluorescent NDs, only a fraction of the substitutional nitrogen impurities are paired with a vacancy during the annealing process. Thus, an improvement in NV^- formation should increase the brightness of an individual ND. Havlik et al. recently conducted a systematic study to optimize annealing temperature and duration for maximum fluorescence intensity.⁹ For nanodiamonds of 140 nm and 45 nm diameters, they found the maximum to occur at 900 °C for 1 hour of annealing. They also found that improved ND surface oxidation increased fluorescence. These efforts, however, were only able to improve ND fluorescence 2.5-fold, and NDs of a comparable size to quantum dots were not studied.

As the size of a fluorescent ND decreases, there are two limits. First, smaller particles have a relatively greater surface area towards which vacancies can migrate during annealing, decreasing the probability of NV^- formation.¹ Second, the stability of the NV^- defect once formed is also size dependent. Bradac et al. studied 5 nm fluorescent NDs produced by detonation and observed intermittency of the luminescence, contrary to the photostability of larger NDs.¹⁰ They attributed the blinking to possible electron traps on the ND surface (which likely contained sp^2 -hybridized carbon) and perhaps also to crystal disorder.

Despite the limited stability of the NV^- defect in small NDs, fluorescent NDs still hold promise to be of interest in the future. Some researchers have begun to look at other fluorescent defects in diamonds, such as the silicon-vacancy defect.¹¹ The NV^- defect is

also of great interest for sensing. Due to the splitting of the spin state, the fluorescence of the NV center can vary with magnetic fields and temperature. Research using fluorescent diamonds for nanoscale NMR¹² and temperature¹³ sensing show some promise, and efforts are being made to bring these applications to nanodiamonds.

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