Creation of high density ensembles of nitrogen-vacancy centers in nitrogen-rich type Ib nanodiamonds

Long-Jyun Su1,5, Chia-Yi Fang1,2,5, Yu-Tang Chang1,2, Kuan-Ming Chen3, Yueh-Chung Yu3, Jui-Hung Hsu4 and Huan-Cheng Chang1,2

1 Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan
2 Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
3 Institute of Physics, Academia Sinica, Taipei 115, Taiwan
4 Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

E-mail: jhsu@mail.nsysu.edu.tw and hchang@gate.sinica.edu.tw

Received 4 February 2013, in final form 27 May 2013
Published 15 July 2013
Online at stacks.iop.org/Nano/24/315702

Abstract
This work explores the possibility of increasing the density of negatively charged nitrogen-vacancy centers ([NV\textsuperscript{−}]) in nanodiamonds using nitrogen-rich type Ib diamond powders as the starting material. The nanodiamonds (10–100 nm in diameter) were prepared by ball milling of microdiamonds, in which the density of neutral and atomically dispersed nitrogen atoms ([N\textsuperscript{0}]) was measured by diffuse reflectance infrared Fourier transform spectroscopy. A systematic measurement of the fluorescence intensities and lifetimes of the crushed monocrystalline diamonds as a function of [N\textsuperscript{0}] indicated that [NV\textsuperscript{−}] increases nearly linearly with [N\textsuperscript{0}] at 100–200 ppm. The trend, however, failed to continue for nanodiamonds with higher [N\textsuperscript{0}] (up to 390 ppm) but poorer crystallinity. We attribute the result to a combined effect of fluorescence quenching as well as the lower conversion efficiency of vacancies to NV\textsuperscript{−} due to the presence of more impurities and defects in these as-grown diamond crystallites. The principles and practice of fabricating brighter and smaller fluorescent nanodiamonds are discussed.

(Some figures may appear in colour only in the online journal)

1. Introduction
The negatively charged nitrogen-vacancy (NV\textsuperscript{−}) defect in diamond is one of the best characterized color centers in the solid state [1–3]. It has recently found wide applications in areas such as single photon generation [4], quantum computing [5], nanoscale magnetic sensing [6, 7], and super-resolution far-field optical microscopy [8]. The center is also appealing for use in bioimaging owing to its unique characteristics of far-red emission and superb photostability [9]. Containing a high density ensemble of NV\textsuperscript{−} centers, fluorescent nanodiamond (FND) is a nanomaterial developed for this application [10, 11]. The material, made of synthetic type Ib diamond, has excellent biocompatibility and exceptionally low toxicity [12, 13]. However, it has not yet received widespread attention in biology and biomedicine because its fluorescence intensity is relatively low compared with those of quantum dots, organic dyes, and fluorescent proteins [14, 15]. The main reason for this is that the absorption cross section of NV\textsuperscript{−} is about 1–2 orders of magnitude smaller than those of organic dyes (or fluorescent proteins) and quantum dots [16, 17]. A way to overcome this deficiency is to increase the density of NV\textsuperscript{−} centers, [NV\textsuperscript{−}], in the particles. If each 10 nm

5 These two authors contributed equally to this work.
FND can contain 10 NV$^-$ centers, which is equivalent to [NV$^-$] $\sim$100 ppm, then the nanomaterial will become highly competitive in the field of bioimaging. However, such a goal is difficult to achieve because the typical density of atomically dispersed nitrogen in most commercially available type Ib diamonds synthesized by high pressure and high temperature (HPHT) methods is 100 ppm. In addition, the conversion efficiency of vacancies created by radiation damage to NV$^-$ (HPHT) methods is 100 ppm. In addition, the conversion efficiency of vacancies created by radiation damage to NV$^-$ is low, typically in the range of 10% [18, 19]. The efficiency is expected to be even lower for nanoscale diamonds, where annealing of vacancies can occur more readily at the surface during annealing [20]. In view of this intrinsically limited conversion efficiency, we propose to use nanodiamond particles with a higher nitrogen density as the starting material to increase [NV$^-$] [10, 21].

Infrared spectroscopy is a commonly used technique to characterize the density of nitrogen in diamond [22]. Figure 1(a) presents a typical infrared absorption spectrum of type Ib bulk diamond. Two prominent features are observed at 1130 and 1344 cm$^{-1}$ and they have been attributed to the localized vibrational modes of C–N bonds [23, 24]. The strengths of these two absorption bands are directly correlated with the density (in ppm) of atomically dispersed nitrogen in the neutral charge state as [22–25]

$$[N^0] = 37.5 \mu_{1344} = 25 \mu_{1130},$$  \hspace{1cm} (1)

where $\mu$ is the absorption coefficient (in cm$^{-1}$) of the sample at the specified wavenumber. This relation provides a foundation for the measurement of [N$^0$] in bulk diamond using infrared spectroscopy. However, it is inapplicable to submillimeter-sized diamond powders, where the sample thickness and hence the absorption coefficient is ill-defined. Liang et al [26] have proposed an alternative based on the ratio of the two absorption coefficients at 1130 and 2120 cm$^{-1}$ as

$$[N^0] = 25 \times 5.5 \times \left( \frac{\mu_{1130}}{\Delta \mu_{2120}} \right),$$  \hspace{1cm} (2)

where $\Delta \mu_{2120}$ is the absorption coefficient difference between the linear line drawn across the two peaks at 2033 and 2160 cm$^{-1}$ and the dip at 2120 cm$^{-1}$ (figure 1(a)). The depth of this dip is characteristic of the two-phonon absorption band of diamond and therefore can be used as an internal standard. However, a complication in this analysis is that an infrared microscope coupled with a Fourier transform infrared (FTIR) spectrometer has to be used in order to acquire the IR absorption spectra of individual diamond microparticles, from which an ensemble average is obtained. The method is time-consuming and laborious and the smallest diamond that can be measured is $\sim$150 $\mu$m in diameter.

To circumvent the aforementioned problems, we have developed a method based on diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), a technique widely used to collect and analyze IR photons scattered from fine particles and powders. The technique has been utilized to characterize the chemical functional groups on diamond surfaces as well [27, 28]. In a study of sonochemical reactions on diamond with DRIFTS, Visbal et al [28] observed the two-phonon absorption band as well as the C–N vibrations for synthetic type Ib diamond powders with grain sizes of 5–12 $\mu$m. For finer particles, the observation at wavenumbers of less than 2000 cm$^{-1}$ was obscured by the absorption of surface functional groups (such as –C–O–C–, –C=O, etc) and/or other adsorbed species after acid washes. In this work, in order to minimize the interference of adsorbate with our measurement, we used particles with size greater than 5 $\mu$m and without any acid treatment. Moreover, we modified equation (2) to

$$[N^0] = 37 \times 5.5 \times \left( \frac{\Delta \mu_{1130}}{\Delta \mu_{2120}} \right),$$  \hspace{1cm} (3)

where $\Delta \mu_{1130}$ is the absorption coefficient difference corresponding to the height of the hump at 1130 cm$^{-1}$ (cf. figure 1(a)). This modification is justified based on the ratio of $\mu_{1130}/\mu_{1280}$ = 3.1 for type Ib bulk diamond [23–26]. The advantage of this modified equation is that the measured [N$^0$] is independent of the sample thickness and also immune to the baseline shift of the DRIFT spectra.
Based on this relationship, we present the result of our effort to fabricate brighter and smaller FNDs using N-rich type Ib diamond powders. By carefully measuring (1) [N\(^0\)] with DRIFTS, (2) fluorescence intensities with a home-built spectrometer, and (3) fluorescence lifetimes with a picosecond laser system, we confirm that the [NV\(^-\)] in type Ib nanodiamonds (~100 nm in diameter) increases with increasing [N\(^0\)] at 100–200 ppm. However, the feature does not hold for as-grown diamonds with a density close to 400 ppm but poorer crystal quality. This result is at variance with a recent report that an enormously high NV concentration of up to 1% can be attained for sintered detonation nanodiamonds with polycrystalline structure [29]. We furthermore developed a new method to crush nanodiamonds into a smaller size in a gentle way. Our results indicate that it is an effective method to produce sub-20 nm nanodiamonds without loss of fluorescence intensity.

2. Experimental section

2.1. Materials

Synthetic microdiamond powders were obtained from three different sources: Element Six (USA), Fine Abrasive Taiwan (Taiwan), and Changsha Naiqiang Superabrasives (China). Five batches of diamonds with different grain sizes were tested and compared, including MDA, YK-J, PK-5, RVD1, and RVD2 (Table 1). Additionally, pristine nanometer-sized diamond particles, Micron + MDA (0–0.1 \(\mu\)m) and MSY (0–0.05 \(\mu\)m) fabricated by Element Six (USA) and Microdiamant (Switzerland), respectively, were used as controls for comparison.

2.2. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

IR spectra of the microdiamond powders were acquired by using an FTIR spectrometer (MB-154, Bomem) equipped with a DRIFT cell (Spectra Tech) and a liquid-nitrogen-cooled HgCdTe (MCT) detector. Crystallites of KBr served as the sample to collect reference spectra. A spectral resolution of 1 cm\(^{-1}\) and a summation of 100 scans were adopted throughout the experiments.

| Name           | Manufacturer   | Size (\(\mu\)m) | [N\(^0\)] (ppm) | Remarks                                      |
|----------------|----------------|----------------|------------------|----------------------------------------------|
| Micron + MDA   | Element Six    | 0–0.1          | UD \(^a\)       | Crushed monocrystalline diamond              |
| MDA            | Element Six    | 8–16           | 120              | Crushed monocrystalline diamond              |
| YK-J           | Fine Abrasive Taiwan | 20–30   | 151              | Crushed monocrystalline diamond              |
| RVD2           | Changsha Naiqiang Superabrasives | 210–250 | 157              | Crushed monocrystalline diamond              |
| RVD1           | Changsha Naiqiang Superabrasives | 210–250 | 209              | Crushed monocrystalline diamond              |
| PK-5           | Fine Abrasive Taiwan | 20–30   | 386              | As-grown virgin diamond                      |

\(^{a}\) Undetermined.

2.3. Ball milling

The microdiamond powders were ground mechanically by using a high-energy shaker mill (8000M, SPEX) [30]. The grinding was conducted in a tungsten carbide (WC) vial containing 5 WC balls (10 mm in diameter). The typical milling time was 30 min.

2.4. Size separation

NDS with size in the range of 100 nm were extracted from the ball-milled microdiamonds by cleaning the particles in mixed aqua regia–hydrogen peroxide solution (1:19, \(v/v\)) heated gently to 85°C for 1 h [31], followed by centrifugal fractionation at 4000 rpm. From repeated sonication and centrifugal separation, a white colloidal solution containing well dispersed ND particles was obtained. The size distributions of the particles were determined by dynamic light scattering using a combined particle size and zeta potential analyzer (Delsa Nano C, Beckman-Coulter).

2.5. Transmission electron microscopy (TEM)

The NDs were transferred to the TEM grid by applying the particle suspension to the grid surface. After being dried in air, they were characterized by using a field emission TEM (Tecnai F20 G2, FEI) operated at 200 keV and equipped with a 2k \(\times\) 2k CCD camera (UltraScan 1000, Gatan).

2.6. FND fabrication

The NDs were radiation-damaged with either a 3 MeV H\(^+\) or a 40 keV He\(^+\) ion beam, as detailed previously [32, 33]. In the first method, a thin diamond film (<50 \(\mu\)m thick) was prepared by depositing ~5 mg of the fine powder on a silicon wafer (1 \(\times\) 1 cm\(^2\)) and subsequently subjected to the ion irradiation at a dose of \(~2 \times 10^{16}\) H\(^+\) cm\(^{-2}\). In the second method, about 70 mg of the powder was deposited on a copper tape (2 m long and 35 mm wide) to form a thin film with an average thickness of ~0.2 \(\mu\)m. The tape rolled in vacuum, allowing the particles to be irradiated continuously by helium ions at a dose of \(~2 \times 10^{15}\) He\(^+\) cm\(^{-2}\). Afterwards, the radiation-damaged diamonds were annealed at 800°C for 2 h to form FNDs. To remove graphitic carbon atoms on the surface, the freshly prepared FNDs were oxidized in air at 490°C for 2 h and microwave-cleaned in concentrated H\(_2\)SO\(_4\)–HNO\(_3\) (3:1, \(v/v\)) at 100°C for 3 h.
2.7. High-pressure crushing

FNDs with size in the range of 30 nm were mixed with NaF powder at a weight ratio of 1:10 and pressed to form a pellet under a pressure of 10 tons by a hydraulic oil press (SPECAC). Next, the pellet was annealed at 720 °C in vacuum for 2 h, after which it was dissolved in hot water to remove NaF.

2.8. Fluorescence spectroscopy

Fluorescence spectra of FNDs suspended in water (typically 1 mg ml$^{-1}$) were acquired by using a setup built in-house [32, 33]. It consisted of two continuous-wave (cw) light sources, i.e. a 532 nm laser (DPGL-2100F, Photop Suwtech) and a 473 nm laser (LDC-1500, Photop Technologies), a set of dichroic beam splitters (Z532RDC, Chroma and FF484-FDi01-25 × 36, Semrock), a long-working distance microscope objective (50×, NA 0.55, Mitutoyo), a long-pass edge filter (E550LP, Chroma), and a multichannel analyzer (C7473, Hamamatsu). Backward fluorescence was collected through the same objective to prevent strong scattering from distorting the spectra.

2.9. Fluorescence lifetime measurement

Fluorescence lifetimes of FNDs suspended in water were measured with a home-built microscope system and a 70 ps, 470 nm pulsed laser (LDH-P-C-470, PicoQuant) [34]. The system consisted of an inverted microscope (IX-71, Olympus) equipped with a dichroic filter (Z473RDC, Chroma) and a 4× objective (UPLSAPO, Olympus), which focused the laser light into the FND suspension in a shallow well mounted on a glass slide. Fluorescence emission was collected by the same objective and guided through two optical filters (HQ485LP, Chroma and NT62-987, Edmund Optics) onto an avalanche photodiode (SPCM-AQR-14-FC, PerkinElmer). Fluorescence lifetime data were recorded by using a photon counting card (SPC-830, Becker–Hickl) and analyzed with SPC-Image software (Becker–Hickl).

3. Results and discussion

3.1. Nitrogen density

Figure 1(b) presents the DRIFT spectrum of RVD1 microdiamonds (particle size of 210–250 µm) and its comparison with the direct IR absorption spectrum of type Ib bulk diamond with [N$^0$] = 109 ppm [16]. In this comparison, the DRIFT spectrum was scaled and shifted so that the two-phonon absorption band of the microdiamond overlapped well with that of the bulk. The difference in the intensities of the absorption bands at 1130 cm$^{-1}$ thus reflects the difference in [N$^0$] between these two samples. In determining [N$^0$] from the spectral comparison, caution has to be taken for the baseline shift of the DRIFT spectra as well as the interference from atmospheric water absorption at 1400–1800 cm$^{-1}$. Use of equation (3) enables us to circumvent the problems and measure [N$^0$] in these microdiamonds with an uncertainty of less than 20%.

Table 1 summarizes the result of the DRIFTS measurements for five diamond samples from three different sources. The [N$^0$] varies widely from 120 ppm for MDA to 386 ppm for PK-5. Moreover, the density varies by up to 50 ppm between batches of the same product (e.g. RVD1 and RVD2 from the same manufacturer). As noted in the table, all samples except PK-5 were produced by crushing high-quality monocrystalline diamonds. PK-5, in contrast, consists of as-grown virgin diamond and therefore can contain a higher density of nitrogen and likely trap more metal impurities from the catalysts used in the HPHT synthesis [35]. A study of the samples with transmission electron microscopy (TEM) revealed that both the MDA and PK-5 nanodiamonds (size ∼100 nm) are monocrystalline in structure but irregular in shape (figures 2(a) and (b)). Some PK-5 particles do contain crystallographic defects such as twin-like structure, as evidenced by the observation of the moiré fringes in figure 2(b) [35].

3.2. Fluorescence intensity

After characterization with DRIFTS the microdiamonds were crushed into finer grains by ball milling, separated by differential centrifugation, and converted into FNDs by ion irradiation and subsequent annealing. Dynamic light scattering measurement indicated that all particles are very similar in size, with a number-averaged diameter of ∼100 nm (figure 3(a)). Figure 3(b) compares the fluorescence spectra of one representative N-rich sample, RVD2, with that of Micron + MDA (0–0.1 µm), suspended in water and excited with a 532 nm laser. As noted, both the NV$^0$ and NV$^-$ centers are identifiable in the spectra based on their distinct zero-phonon lines (ZPLs) at 575 nm and 638 nm, respectively [36, 37]. For the 100 nm FNDs prepared with crushed monocrystalline microdiamonds (such as MDA, YK-J, RVD1, and RVD2 listed in table 1), we did observe a trend of fluorescence intensity increase with increasing [N$^0$] (figure 4(a)). However, the trend failed to continue for
samples, such as PK-5, with higher \([N^0]\) but poorer crystal quality. Depending on the irradiation treatment (either 40 keV He\(^+\) or 3 MeV H\(^+\)), the fluorescence intensity of this sample is only comparable to or even lower than that of MDA (and also Micron + MDA), although its nitrogen density is more than three times as high.

The dose of the 3 MeV H\(^+\) irradiation used in this experiment was \(\sim 2 \times 10^{16}\) protons cm\(^{-2}\), which resulted in an estimated damage density of \(\sim 2 \times 10^{19}\) vacancies cm\(^{-3}\) [16, 38]. Similar damage densities were achieved with the 40 keV He\(^+\) irradiation [32, 33]. We attempted to increase the dose by a factor of 2 but did not observe significant change in the fluorescence intensity. The result is in agreement with the report of Walderrmann et al [39] who used 2 MeV He\(^+\) irradiation to create high density ensembles of NV\(^-\) in type Ib bulk diamond and found that the optimum damage density for the formation of optically accessible NV\(^-\) is \(\sim 3 \times 10^{19}\) vacancies cm\(^{-3}\). In figure 4(a), the reason why there is a \(\sim 2\)-fold difference in fluorescence intensity between these two sets of data is perhaps the fact that the 3 MeV H\(^+\) can penetrate much deeper in diamond than 40 keV He\(^+\), i.e. 50 \(\mu\)m versus 0.20 \(\mu\)m [38], which makes it easier to ensure that all particles are irradiated. Moreover, the irradiation is much gentler (\(\sim 100\times\) lower ion flux [32]), resulting in less amorphization of the diamond matrix. The latter can lead to fluorescence quenching and thus reduction of the fluorescence lifetime as discussed below.

### 3.3. Fluorescence lifetime

A possible cause for the marked decline of the fluorescence intensity at \([N^0] = 386 ppm\) in figure 4(a) is that the fluorescence quantum yield (\(Q_F\)) decreases with increasing \([N^0]\). The yield is related to the radiative and non-radiative decay rates, \(k_r\) and \(k_{nr}\) respectively, of the NV\(^-\) center by

\[
Q_F = \frac{k_r}{k_r + k_{nr}} = k_r \tau.\tag{4}
\]

Since \(k_c\) is a constant, measuring the fluorescence lifetime (\(\tau\)) thus provides a means to verify this possibility. Shown in figure 3(c) are typical fluorescence decay time traces of two FND samples prepared by using either 40 keV He\(^+\) or 3 MeV H\(^+\) irradiation for the same MDA diamond. In this experiment, the fluorescence lifetimes were also measured.
for FNDs suspended in water to obtain ensemble averages. A picosecond laser operating at 470 nm and 5 MHz excited the NV center, which has a phonon sideband extending to ∼450 nm [36]. The resulting fluorescence was collected at a wavelength of λ_{em} > 700 nm to avoid detection of the signal (<20%) from NV^0, which has a significantly longer emission lifetime than NV^- (19 ns [40] versus 11.6 ns [41]) in synthetic type Ib bulk diamond. The observed fluorescence lifetime trace was then fitted with a double-exponential decay function, I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2), from which the intensity-weighted mean lifetime (\tau_i) was calculated as

\[ \tau_i = \frac{a_1 \tau_1^2 + a_2 \tau_2^2}{a_1 \tau_1 + a_2 \tau_2}. \]  

Figure 4(b) shows the measured lifetimes of ten FND samples and their [N^3] dependences. For the 3 MeV H^+ irradiation, the longest lifetime observed for the four crushed monocrystalline nanodiamonds in water is \tau_i ∼ 17 ns for MDA, which has the lowest [N^3]. The lifetime, however, substantially decreases to ∼11 ns for PK-5, the as-grown virgin diamond. Similar results were obtained for FNDs prepared by using the 40 keV He^+ irradiation, although their corresponding lifetimes are all systematically shorter by ∼20%.^6^ The variation of the fluorescence lifetimes shown in figure 4(b) should not be associated with a change in refractive index of the surrounding medium of the NV^- centers [42, 43], since the FND particles used in these measurements are all similar in size (figure 3(a)) and were examined under the same conditions. Rather, it is more likely to be a result of fluorescence quenching due to the presence of more impurities (such as nitrogen atoms and metal inclusions) and defects (such as twins, dislocations, etc) in these as-grown diamond crystals (figure 2(b)). It is noted that the observed lifetime shortening alone is not sufficient to account for the large intensity decrease of PK-5. If we assume that the measured fluorescence intensity (I) is linearly proportional to [NV^-] and Q_F as I ∝ [NV^-] \cdot Q_F, then [NV^-] ∝ I/Q_F ∝ I/\tau,

\[ \text{and } \tau_i = a_1 \tau_1 + a_2 \tau_2/a_1 + a_2. \]

According to equation (4). With the measurements of both I and \tau for the individual samples, it is possible to determine the relative density of NV^- among the FND particles. Figure 4(c) presents the results of the analysis, where the relative [NV^-] is seen to increase nearly linearly with increasing [N^0] at 100–200 ppm for crushed monocrystalline diamonds. In contrast, the [NV^-] of PK-5 is much lower than expected, despite it containing up to 390 ppm of atomic nitrogen. It is speculated that the presence of structural defects in the as-grown diamond has a profound effect on the NV formation since they will reduce the conversion efficiency of N^0 → NV^- through vacancy annihilation at different types of host–defect interfaces. Such an effect is anticipated to be more prominent for detonation nanodiamonds, which are polycrystalline in structure and contain a higher density of impurities [44, 45]. We conclude from the systematic intensity as well as lifetime measurements that it is the combination of the lower fluorescence quantum yield and the less efficient production of NV^- that results in the weaker fluorescence as observed experimentally for PK-5 in figure 4(a).

3.4. NV^0 versus NV^- 

For the formation of NV^- in radiation-damaged type Ib diamond, the widely accepted mechanism is that it involves a two-step reaction as [46, 47]

\[ V^0 + 2N^0 \rightarrow NV^0 + N^0 \rightarrow NV^- + N^+. \]  

In the second reaction, an additional electron donor located in the vicinity of NV^0 is required to convert this defect into its negatively charged state, NV^-.

\[ \text{The present study of the [N^0] dependence provides a test ground for the theory. By comparing the fluorescence intensities of the bands at 575 nm (contributed mainly by the NV^0 centers) and 750 nm (contributed mainly by the NV^- centers) in figure 3(b), we obtained an intensity ratio of } I_{575}/I_{750} \sim 0.4 \text{ for the MDA diamond with } [N^0] = 120 \text{ ppm. The ratio, however, decreased noticeably to } \sim 0.2 \text{ when } [N^0] \text{ increased to 386 ppm (figure 5(a)), implying a decrease in the relative density of } NV^0 \text{ versus } NV^- \text{. To enhance the observation of this effect, a 473 nm laser was used to acquire the fluorescence spectra.} \]
The laser preferentially excites NV\(^0\), thereby improving its fluorescence intensity (figure 5(b)). Plotting \(I_{575}/I_{750}\) against [N\(^0\)] yields results in agreement with those of the 532 nm excitation for samples prepared with either H\(^+\) or He\(^+\) irradiation. Such a distinct [N\(^0\)] dependence of [NV\(^0\)]/[NV\(^-\)] supports the reaction mechanism illustrated in equation (6).

According to the above mechanism, the highest achievable [NV\(^-\)] is 50 ppm for diamond containing 100 ppm of N\(^0\). Additionally, the [NV\(^-\)] should increase with [N\(^0\)] if sufficient vacancies have been supplied by the ion irradiation. This leads to an interesting question: what is the highest possible density of NV\(^-\) in type Ib nanodiamond? In a study on the change of the absorption spectra of type Ib bulk diamond by heavy neutron irradiation, Mita [37] observed that the [NV\(^-\)] increases linearly with the irradiation dose up to \(7 \times 10^{17}\) neutrons cm\(^{-2}\) and then decreases. At this optimum dose, the diamond with [N\(^0\)] = 128 ppm showed an absorption band peaking at \(~560\) nm with an absorption coefficient of \(~260\) cm\(^{-1}\) at 532 nm. This coefficient along with the absorption cross section of \(\sigma_b = 3.1 \times 10^{-17}\) cm\(^2\) [16] for NV\(^-\) in bulk diamond yields [NV\(^-\)] = 48 ppm. This density is much higher than the 25 ppm estimated by Wee et al [16], 6.3 ppm measured by Aharonovich et al [48], and 13.5 ppm reported more recently by Botsoa et al [49]. However, it should be taken as the upper limit of the density since complete conversion of the radiation-generated vacancies (V\(^0\) and V\(^-\)) to NV\(^-\) during thermal annealing had been assumed when estimating [NV\(^-\)] by Davies et al [50]. Nonetheless, the density is likely to be achieved by use of N-rich diamond.

### 3.5 Size reduction

Having both high [NV\(^-\)] and high \(Q_F\), the FNDs fabricated with RVD2 diamonds meet the requirements for practical use in bioimaging. If one makes a reasonable estimation for the conversion efficiency of N\(^0\) → NV\(^-\) to be \(~20\)%, the N-rich 100 nm diamonds can then contain up to 30 ppm of NV\(^-\) or \(~3000\) NV\(^-\) fluorophores per particle. Detection of these bright FND particles individually on a glass coverslip or even in cells is feasible with commercial confocal fluorescence microscopes [51]. For real-world applications as biolabels, the FNDs should be made as small as possible [52]. These particles can either be produced by crushing 100 nm FNDs into smaller parts with the ball-milling technique or be made from smaller pristine NDs treated with ion irradiation and annealing as described earlier. Figure 6(a) compares the fluorescence spectra of 30 nm and 35 nm FNDs, prepared by using these two different methods, with that of 100 nm FNDs as the reference sample. For the 30 nm FNDs prepared by ball milling, a 2-fold loss in fluorescence intensity (on the same weight basis) results, which is in large part due to the decrease of the fluorescence lifetime (and hence quantum yield) from \(\tau_i = 17\) ns to \(\tau_i = 13\) ns (figure 6(b)). Compared with the 7-fold decrease in fluorescence intensity for FNDs prepared directly from pristine 35 nm nanodiamonds, the loss is clearly more acceptable.

It is tempting to fabricate smaller FNDs using the same ball-milling technique. Indeed, particles with diameters in the range of 15 nm can be produced, but their fluorescence intensity is \(~10\)-fold lower than expected (on the same weight basis). This could be a result of surface-induced vacancy annihilation and crystal amorphization, both of which can occur more readily during ball milling of smaller FNDs. To overcome this hurdle, a method utilizing a hydraulic oil press to crush ball-milled 30 nm FNDs under a pressure of 10 tons was developed (as described in section 2.7). The method is gentle and effective with a typical production yield of \(~60\)% for sub-20 nm FNDs. Included in figure 6(a) is the fluorescence measurement for 18 nm FNDs, whose fluorescence intensity and spectral profile are essentially unchanged after crushing. To further reduce the particle size to the sub-10 nm range without the loss of NV\(^-\), oxygen etching techniques as described by Mohan et al [15] and Gaebel et al [53] could be used.

### 4. Conclusion

We have successfully fabricated FNDs containing high density ensembles of NV\(^-\) centers in diamond nanoparticles

---

**Figure 6.** Comparison of the fluorescence intensities (a) and lifetimes (b) of FNDs with different sizes. The 100 nm and 35 nm FNDs were prepared from pristine NDs, the 30 nm FNDs were produced by ball milling of 100 nm FNDs, and the 18 nm FNDs were fabricated by crushing of 30 nm FNDs with a hydraulic press. The concentration of all FND suspensions is 1 mg ml\(^{-1}\).
of various sizes (10–100 nm) using N-rich type Ib diamond powders as the starting material. We demonstrate that it is possible to improve the brightness of FNDs with the [N]$^-$ concentration from 100 ppm to 200 ppm for crushing monocrystalline diamonds. Our results indicate that through careful control of the radiation damage conditions and proper choice of the diamond materials, increase of [NV$^-$] above 10 ppm in 10 nm FND particles is practical.

Acknowledgments

This work is supported by Academia Sinica and the National Science Council of Taiwan with Grant Nos 99-2119-M-001-026 and 100-2112-M-110-002. We thank Ella Yang at Changsha Naiqiang Superabrasives for providing diamond samples and L-C Wang for taking the TEM images.

References

[1] Jelezko F and Wrachtrup J 2006 Single defect centers in diamond: a review. Phys. Status Solidi a 203 3207–25
[2] Aharonovich I, Castelletto S, Simpson D A, Su C H, Greenstreet A D and Prawer S 2011 Diamond-based single-photon emitters Rep. Prog. Phys. 74 076501
[3] Aharonovich I, Greenstreet A D and Prawer S 2011 Diamond photonics Nature Photon. 5 397–405
[4] Kurtsiefer C, Mayer S, Zarda P and Weinfurter H 2000 Stable solid-state source of single photons Phys. Rev. Lett. 85 290–3
[5] Dutt M V G, Childress L, Jiang L, Togan E, Maze J, Jelezko F, Kiflawi I, Mayer A E, Spear P M, van Wyk J A and Collins A T 1990 The nitrogen-content of type-1b synthetic diamond Phil. Mag. B 62 589–95
[6] Baranov P G, Ando T, Inoue S, Ishii M, Kamo M, Sato Y, Yamada O and Nakano T 1993 Fourier-transform infrared photoacoustic studies of hydrogenated diamond surfaces J. Chem. Soc. Faraday Trans. 89 749–51
[7] Kandal G, Curmi P A and Treussart F 2009 Comparison of the diffusion of diamond nanoparticles in living cells Nano Lett. 10 144–7
[8] Jung Z Z, Jia X, Ma H A, Yang L, Chen Y Y, Hui Y Y, Cheng C L and Chang H C 2010 Sub-20-nm fluorescent nanodiamonds as photostable biolabels and fluorescence resonance energy transfer donors Adv. Mater. 22 843–7
[9] Wee T L, Tzeng Y K, Han C C, Chang H C, Fann W, Hsu J H, Chen K M and Yu Y C 2007 Two-photon excited fluorescence of nitrogen-vacancy centers in proton-irradiated type Ib diamond J. Phys. Chem. A 111 9379–86
[10] Chapman R and Plakhotnik T 2011 Quantitative luminescence microscopy on nitrogen-vacancy centers in diamond: saturation effects under pulsed excitation Chem. Phys. Lett. 507 190–4
[11] Vaijayanthimala V and Chang H C 2009 Preparation and characterization of green fluorescent nanodiamonds for biological applications Nanotechnology 20 235602
[12] Vaijayanthimala V, Tzeng Y K, Jelezko F, Wrachtrup J and Meijer J 2010 Creation efficiency of nitrogen-vacancy centres in diamond New J. Phys. 12 065017
[13] Smith B R, Inglis D W, Sandnes B, Rabeau J R, Zvyagin A V, Gruber D, Noble C J, Vogel R, Osawa E and Plakhotnik T 2009 Nanoindentation of type Ib diamond with luminescent nitrogen-vacancy defect centers Small 5 1649–53
[14] Mohan N, Tzeng Y K, Jelezko F, Wrachtrup J, Aubert P, Sennour M, Balasubramanian G, Reuter R, Thorel A and Gaffet E 2009 High yield fabrication of fluorescent nanodiamonds Nanotechnology 20 235602
[15] Ando T, Inoue S, Ishii M, Kamo M, Sato Y, Yamada O and Nakano T 1993 Fourier-transform infrared photoacoustic studies of hydrogenated diamond surfaces J. Am. Chem. Soc. 127 17604–5
[16] Baranov P G et al 2011 Enormously high concentrations of fluorescent nitrogen-vacancy centers fabricated by sintering of detonation nanodiamonds Small 7 1533–7
[17] Silva K L, Bernardi L O, Yokoyama M, Trombini V, Zeng Y K and Chang H C 2011 Nonblinking green emission from single H3 color centers in nanodiamonds Appl. Phys. Lett. 98 193116
[18] Vaijayanthimala V, Tzeng Y K, Jelezko F, Wrachtrup J and Meijer J 2010 Creation efficiency of nitrogen-vacancy centres in diamond New J. Phys. 12 065017
[19] Smith B R, Inglis D W, Sandnes B, Rabeau J R, Zvyagin A V, Gruber D, Noble C J, Vogel R, Osawa E and Plakhotnik T 2009 Nanoindentation of type Ib diamond with luminescent nitrogen-vacancy defect centers Small 5 1649–53
[20] Mohan N, Tzeng Y K, Jelezko F, Wrachtrup J, Aubert P, Sennour M, Balasubramanian G, Reuter R, Thorel A and Gaffet E 2009 High yield fabrication of fluorescent nanodiamonds Nanotechnology 20 235602
[21] Ando T, Inoue S, Ishii M, Kamo M, Sato Y, Yamada O and Nakano T 1993 Fourier-transform infrared photoacoustic studies of hydrogenated diamond surfaces J. Chem. Soc. Faraday Trans. 89 749–51
[22] Visbal H, Ishizaki C and Ishizaki K 2004 Ultrasonic treatment of acid-washed diamond powder surface J. Ceram. Soc. Japan 112 95–8
[23] Baranov P G et al 2011 Enormously high concentrations of fluorescent nitrogen-vacancy centers fabricated by sintering of detonation nanodiamonds Small 7 1533–7
[24] Silva K L, Bernardi L O, Yokoyama M, Trombini V, Zeng Y K and Chang H C 2011 Nonblinking green emission from single H3 color centers in nanodiamonds Appl. Phys. Lett. 98 193116
[35] Yin L W, Li M S, Cui J J, Bai Y J, Xu B, Gong J H and Hao Z Y 2002 Planar defects and dislocations in HPHT as-grown diamond crystals Diamond Relat. Mater. 11 268–72
[36] Davies G and Hamer M F 1976 Optical studies of 1.945 eV vibronic band in diamond Proc. R. Soc. A 348 285–98
[37] Mita Y 1996 Change of absorption spectra in type-1b diamond with heavy neutron irradiation Phys. Rev. B 53 11360–4
[38] www.srim.org/
[39] Waldermann F C et al 2007 Creating diamond color centers for quantum optical applications Diamond Relat. Mater. 16 1887–95
[40] Liaugaudas G, Davies G, Suhling K, Khan R U A and Evans D J F 2012 Luminescence lifetimes of neutral nitrogen-vacancy centres in synthetic diamond containing nitrogen J. Phys.: Condens. Matter 24 435503
[41] Collins A T, Thomaz M F and Jorge M I B 1983 Luminescence decay time of the 1.945 eV center in type 1b diamond J. Phys. C: Solid State Phys. 16 2177–81
[42] Beveratos A, Brouri R, Gacoin T, Poizat J P and Grangier P 2001 Nonclassical radiation from diamond nanocrystals Phys. Rev. A 64 061802
[43] Tisler J et al 2010 Fluorescence and spin properties of defects in single digit nanodiamonds ACS Nano 3 1959–65
[44] Vlasov I I, Shenderova O, Turner S, Lebedev O I, Basov A A, Sildos I, Rähn M, Shiryav A A and Van Tendeloo G 2010 Nitrogen and luminescent nitrogen-vacancy defects in detonation nanodiamond Small 6 687–94
[45] Bradac C, Gaebel T, Naidoo N, Sellars M J, Twamley J, Brown L J, Barnard A S, Plakhotnik T, Zvyagin A V and Rabeau J R 2010 Observation and control of blinking nitrogen-vacancy centres in discrete nanodiamonds Nature Nanotechnol. 5 345–9
[46] Collins A T 2002 The Fermi level in diamond J. Phys.: Condens. Matter 14 3743–50
[47] Collins A T, Connor A, Ly C H, Shareef A and Spear P M 2005 High-temperature annealing of optical centers in type-1 diamond J. Appl. Phys. 97 083517
[48] Aharonovich I, Santori C, Fairchild B A, Orwa J, Ganesan K, Fu K M C, Beausoleil R G, Greentree A D and Prawer S 2009 Producing optimized ensembles of nitrogen-vacancy color centers for quantum information applications J. Appl. Phys. 106 124904
[49] Botsoa J, Sauvage T, Adam M P, Desgardin P, Leoni E, Courtois B, Treussart F and Barthe M F 2011 Optimal conditions for NV- center formation in type-1b diamond studied using photoluminescence and positron annihilation spectroscopies Phys. Rev. B 84 125209
[50] Davies G, Lawson S C, Collins A T, Mainwood A and Sharp S J 1992 Vacancy-related centers in diamond Phys. Rev. B 46 13157–70
[51] Zhang B, Li Y, Fang C Y, Chang C C, Chen C S, Chen Y Y and Chang H C 2009 Receptor-mediated cellular uptake of folate-conjugated fluorescent nanodiamonds: a combined ensemble and single-particle study Small 5 2716–21
[52] Fu C C, Lee H Y, Chen K, Lim T S, Wu H Y, Lin P K, Wei P K, Tsao P H, Chang H C and Fann W 2007 Characterization and application of single fluorescent nanodiamonds as cellular biomarkers Proc. Natl Acad. Sci. USA 104 727–32
[53] Gaebel T, Bradac C, Chen J, Say J M, Brown L, Hemmer P and Rabeau J R 2011 Size-reduction of nanodiamonds via air oxidation Diamond Relat. Mater. 21 28–32