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Characterization of nanodiamonds for metamaterial applications

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Abstract Several different types of nanodiamonds were characterized in order to find the best sample to be used in further experiments with metamaterials. In this work we present the results of optical analysis of aqueous suspensions containing nanodiamonds, SEM analysis of diamond particles dispersed on silicon substrates and measurements of photoluminescence from defects in nanodiamonds.

1 Introduction

Diamond is a true gift of nature and is well known as the hardest natural material. It is widely used in the jewellery and abrasion industries. Several decades ago, renewed scientific interest arose for diamonds. In particular, scientific attention was focused on crystallographic defects in diamonds. One of the most interesting defects from the point-of-view of applications is nitrogen-vacancy (NV) color cen-

ter. These color centers in diamond produce stable, broadband, room-temperature, and anti-bunched fluorescence [1, 2]. This amazing feature opens up possibilities for a large variety of applications in quantum information processing such as single-photon sources [3], biomarking [4], and high-resolution magnetic [5] and electric [6] field sensing.

The applications listed above could benefit from an increased flux of single photons, which can be achieved by engineering the electromagnetic environment of the emitter. It has been already demonstrated that such enhancement could be accomplished by coupling NV-centers in diamond with photonic crystal [7] and plasmonic cavities [8], creating monolithic diamond architectures like solid immersion lenses [9] and nanowires [10]. However, there is still a need for increasing the single-photon flux in a broad spectral range, beyond the reach of the techniques used so far. Coupling NV-centers to metamaterials could be helpful in achieving this goal [11]. As an effort in this direction, we have studied the properties of various diamond samples in order to determine their suitability for such applications.

It is also important to note that diamond's high refractive index seriously limits the fraction of luminescence that can be extracted from a flat interface. This problem could be partially solved by using nanodiamonds, which are nanometer-scale diamond particles containing one or a few NV-centers, instead of bulky nanoscale grains. Because the collection efficiency could be improved using nanodiamonds, they are our choice of material in our studies. In this work we characterize several types of nanodiamonds prepared by different methods in order to find the best samples for use in further experiments with metamaterials.

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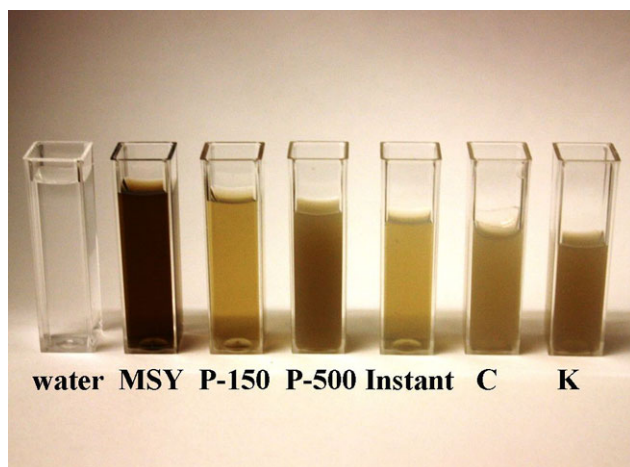


Fig. 1 Deionized water and aqueous suspensions of nanodiamonds: MSY, “P-150”, “P-500”, “Instant”, “C”, “K”. The concentration of nanodiamonds in all suspensions is 0.1 wt%

2 Experimental details

2.1 Samples

We studied six different types of nanodiamonds in this work (see Fig. 1). The first type is a monocrystalline synthetic diamond (MSY) material produced by high-pressure, high-temperature (HPHT) synthesis. These nanodiamonds were purchased from Microdiamant AG in aqueous suspension. The median size of the diamonds claimed by the manufacturer is 18 nm. The initial concentration of the diamonds in the suspension was 1 wt%. The suspension was diluted to 0.1 wt%. It should be mentioned that this is the only sample studied in this work which was purchased in the form of aqueous suspension.

Apart from MSY, the other nanodiamond samples were created via a standard detonation process and were additionally processed by removing surface contamination and fractionated [12]. These nanodiamonds are denoted as “P-150” and “P-500” in this work, and they have aggregate sizes ranging from 0–125 nm and from 150–400 nm, respectively. The powders were suspended (0.1 wt%) in deionized water. These samples (“P-150” and “P-500”) can be easily dispersed in water and hence, no ultrasonication was applied.

Samples denoted “C” and “K” (Fig. 1) are detonation nanodiamonds manufactured by RFNC-VNIITF (Russia) and by PLC “ATM” (Russia), respectively. The nanodiamond sample named “Instant” is the result of modification of sample “K” by Advan Solutions, Inc. (USA). The corresponding aqueous suspensions of samples “C”, “K”, and “Instant” (at 0.1 wt%) were prepared with ultrasonication.

For characterization of the nanodiamond samples by scanning electron microscope (SEM) and investigations of nanodiamond photoluminescence (PL) properties, the available aqueous suspensions were spin-coated onto clean cov-

erslips and silicon substrates at 2000 rpm for 3 minutes. The substrates were precleaned with piranha acid solution.

2.2 Experimental setup

A Branson Sonifier Cell Disruptor W-350 was used for powerful ultrasonication in preparing the aqueous suspensions containing “Instant”, “K”, and “C”. The ultrasonication procedure consisted of 10 cycles, with each cycle lasting approximately 6 min and consisting of 1 min of ultrasonication and 5 min of ice cooling. The ultrasonic power was 100 W, and the power density was enhanced by a 1/8-inch tip.

The optical spectra of the nanodiamond suspensions were measured with a Lambda 950 spectrophotometer (Perkin Elmer). Scanning electron microscope images were obtained with a Hitachi S4800 Field-Emission SEM. The observations and spectral measurements of the nanodiamond photoluminescence were carried out with a modified compound Raman microscope [13]. The 543-nm line of a HeNe laser was used to excite the defect centers in the nanodiamonds. The excitation power was about 0.15 mW. The emitted light was collected by 60 × water immersion (NA 1.2) objective (UPlanApo/IR, Olympus) and detected with a photomultiplier tube (PMT) detector (H7422-40, Hamamatsu). For measuring the photoluminescence spectra, we have used a spectrometer (Shamrock SR-303i-A, Andor Technology) equipped with a 300 grooves/mm 500-nm blaze angle grating and a thermoelectrically cooled CCD camera (Newton DU920N-BR-DD). In the signal path we used a 575-nm longpass filter to block the excitation light and a pinhole to create confocal configuration to reduce the background light.

3 Characterization of nanodiamonds

This work was intended to characterize the available nanodiamond samples. In this section we present the results of optical analysis of aqueous suspensions containing nanodiamonds, SEM analysis of nanodiamond particles dispersed on silicon substrates, and measurements of photoluminescence from defects in the nanodiamond samples.

3.1 Optical analysis of suspensions

In order to obtain the optical spectra (Fig. 2) in the visible range (350–800 nm) the nanodiamond suspensions were loaded into 1 cm × 1 cm plastic cuvettes (Starna Cells, Inc.) and measured using a Lambda 950 spectrophotometer. Comparing the scattering spectra of the suspensions (Fig. 2b) to the scattering spectrum of deionized water, we see that all types of nanodiamonds in suspension form large agglomerations except MSY. If the nanodiamond particles

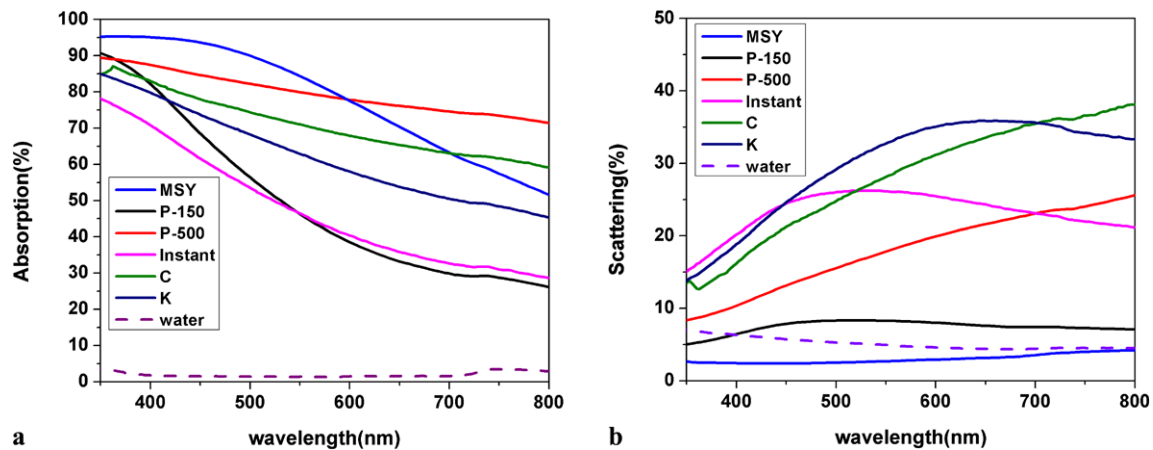


Fig. 2 (a) Absorption and (b) scattering spectra of deionized water and aqueous suspensions (0.1 wt%) of available nanodiamonds: MSY, “P-150”, “P-500”, “Instant”, “C”, and “K”, in the visible range (350–800 nm)

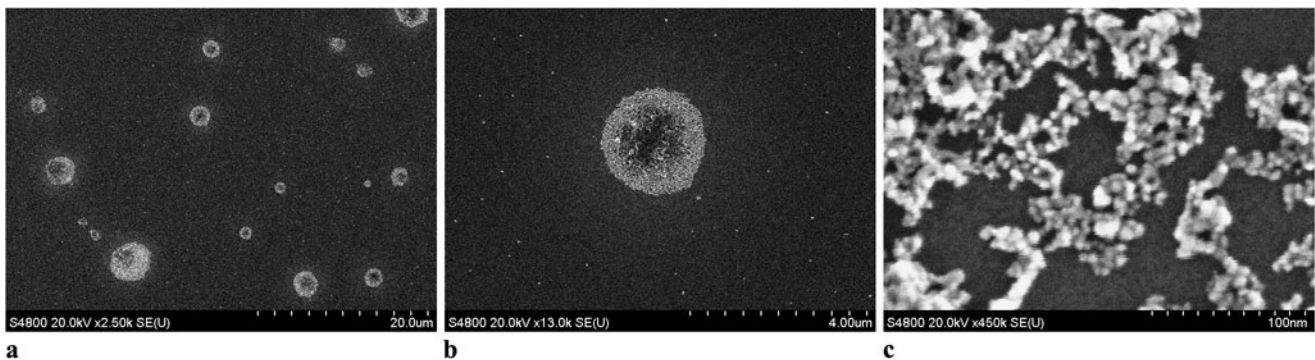


Fig. 3 SEM images of “P-500” nanodiamonds on Si wafer: (a) large agglomerations ($>0.5 \mu\text{m}$) exist, (b) a large number of small (about 10–40 nm) particles are observed around agglomeration centers, (c) agglomerations consist of single particles with sizes of about 10–25 nm

were not agglomerated, the scattering in the suspensions would be negligible compared to that of water. Since this is not the case, we conclude that the nanodiamond particles are agglomerated except for the MSY sample. The exact size distribution of agglomerations cannot be determined from spectral measurements because the absorption spectrum is different for each type of suspension. The reason for the low scattering measured in MSY could be high absorption (Fig. 2a).

These spectral measurements were repeated after one month, during which time the samples were stored under normal darkroom conditions. The suspensions MSY, “P-150”, “P-500”, and “Instant” turned out to be the most stable, and almost no changes in spectra were noticed.

3.2 SEM analysis of nanodiamonds dispersed on a Si substrate

We performed SEM analysis of the samples in order to investigate the size distributions and densities of the nanodiamond agglomerations. The nanodiamond suspensions

were dispersed onto Si wafers and imaged at normal incidence. The details of the sample preparation are discussed in Sect. 2.1. Representative SEM images are shown in Fig. 3.

From the SEM images, samples MSY, “P-150”, “P-500” (Fig. 3), “Instant”, and “K” contain a large number of small diamond particles with sizes of about 10–40 nm as well as agglomeration centers with maximum sizes of about 5 μm . The “C” nanodiamonds are heavily agglomerated, and no single small particles were observed.

3.3 Observation of photoluminescence

Diamond is known to contain crystallographic defects, some of which are fluorescent [14]. Nitrogen-vacancy (NV) color centers in diamond are of particular interest because they could enable a number of promising applications [3–6]. Usually, NV-centers are formed by irradiation with high-energy charged particles followed by annealing above 700°C. The nanodiamonds studied in this work were neither irradiated nor annealed. However, NV-centers are still expected to exist naturally within the nanodiamonds but with

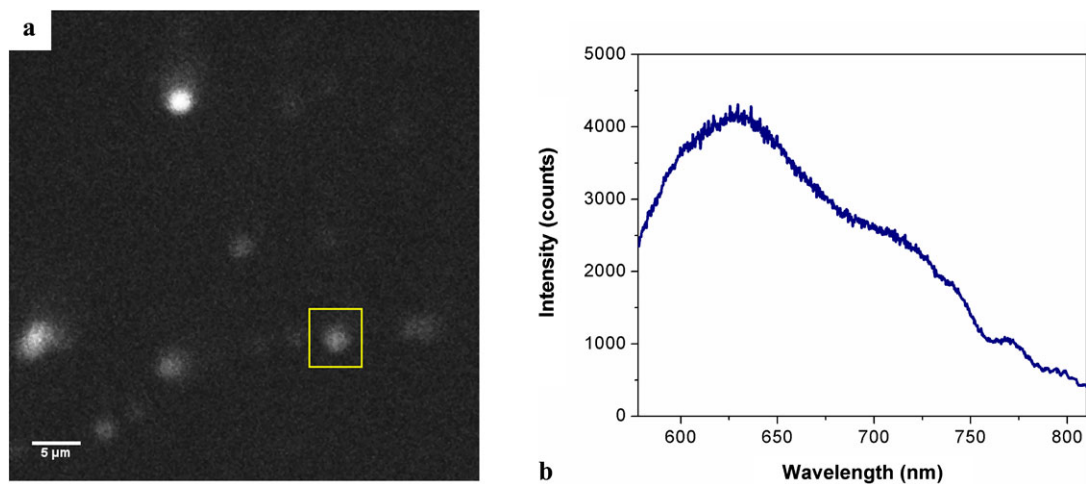


Fig. 4 (a) Photoluminescence microscopy image and (b) emission spectrum of “P-500” nanodiamonds distributed on a coverslip. Excitation is from a HeNe laser at 543 nm and of 0.15-mW power

lower concentrations. Among the available samples, photoluminescence (PL) signals were observed from MSY, “P-150”, and “P-500”. Nevertheless, stable PL was observed only in case of “P-500” (see Fig. 4a).

The PL spectrum of the nanodiamond cluster marked in Fig. 4a is shown in Fig. 4b. The maximum of the broadband signal is about 630 nm. Comparing with the spectra of the NV-centers in bulk diamonds [10, 15], or in nanodiamonds with sizes much larger than 10–20 nm [16, 17], our measured PL spectrum of “P-500” is shifted by approximately 50 nm to shorter wavelengths. Similar results were previously observed for ultra-fine nanodiamonds by several groups. The reason for this shift could be the size effect [16] or surface defects [18]. Further investigation is required in order to identify the exact role of NV-centers in the measured PL signal.

4 Conclusion

In summary, six different types of nanodiamonds were characterized by several different techniques. The “P-150” and “P-500” nanodiamonds can be dispersed easily in water, but others require powerful ultrasonication. In general, the nanodiamond suspensions MSY, “P-150”, “P-500”, and “Instant” were found to be stable for many weeks. All samples except “C” contain a large number of small (10–40 nm) nanodiamond particles. The nanodiamond sample “P-500” showed a good fluorescence signal, which could be useful for quantum optical applications. Stable, bright single-photon sources such as NV-centers in nanodiamonds could pave the way for quantum-optics with metamaterials.

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