

Article

Observation and Analysis of Luminescence of a Colloidal-Organized Suspension of Nanodiamond

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Abstract

This paper investigates the spectral properties of colloiddally ordered systems formed from 100 nm nanodiamonds (NDs) synthesized using the high-pressure high-temperature (HPHT) method. Despite the polydispersity and irregular shape of the particles, aqueous ND suspensions can colloiddally order via repeated centrifugation-induced sedimentation. To the best of our knowledge, this is the first spectroscopic study of such ordered ND systems. In our study, we obtained colloiddally ordered ND structures, evidenced by the formation of rainbow-colored layers in the centrifuge tubes. Fragments extracted from these layers were subjected to microscopic and spectroscopic characterization. Spectroscopic measurements with 488 nm wavelength laser reveal modulated emission in a narrower spectral range, lying within the characteristic broad emission band of NDs and indicating the formation of ordered structures with a characteristic micrometer scale. In view of the intrinsic luminescence of NDs, we propose that these structures are best regarded as analogous to colloidal photonic crystals with intrinsic luminescence. This concept can significantly extend the functionality of ND-based materials and offers new opportunities for fundamental optical studies and practical photonic applications.

Keywords: nanodiamond; colloid crystal; luminescence; photonic crystal; colloidal-ordered structures; iridescence; selective reflection; scattering; internal emission; nanoparticles

1. Introduction

Nanodiamonds (NDs) are a class of versatile materials whose tunable properties render them suitable for a broad range of applications, including electronics, optoelectronics, spintronics, catalytic chemistry, composite and tribological materials engineering, biotechnology, and biomedicine [1–5].

The luminescent properties of NDs are crucial for many of these applications. The optical bandgap of diamond is very large, about 5.5 eV; thus, ND photoluminescence originates primarily from a wide variety of color centers, as well as from non-diamond surface inhomogeneities and recombination processes [6–10]. For NDs, the factors influencing their photoluminescence are considered from both fundamental and applied research perspectives. Accordingly, various methods have been proposed to regulate their photoluminescence in order to optimize the performance across different applications fields.

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These strategies include modifying the crystal lattice structure (e.g., creating color centers that can be excited and emit in desired spectral regions [8,11–13]), surface functionalization and modification [10,14,15], low-temperature annealing [15–17], and other approaches.

One of the interesting but poorly studied properties of NDs is the ability of their suspensions, under proper conditions, to form colloidal-ordered structures with a rainbow-like color distribution, as well as the capability of such structures to selectively interact with light. The formation of colloidal crystals that selectively interact with light is widely discussed, typically for highly monodisperse suspensions of spherical particles (e.g., latex/polymer or silica beads) [18–21]. This type of ordering of diamond nanoparticles, which, unlike those mentioned above, are irregularly shaped particles with an extremely low degree of monodispersity (i.e., highly polydisperse), was first demonstrated using detonation nanodiamonds (DND) [22]. Later, the formation of self-assembled centimeter-scale photonic structures was also mentioned in a colloidal suspension of 100 nm NDs synthesized using the high-pressure high-temperature method (HPHT) NDs [23]. In fact, these two studies remain the sole reports on ordered nanodiamond colloidal systems with characteristic dimensions on the order of optical wavelengths. While they explored light scattering governed by the colloidal structure and particle spatial arrangement, the spectral properties of these systems, which exhibit photonic-crystal-like characteristics, were not investigated.

With regard to NDs, it is also worth noting the few studies concerning the properties of systems obtained from DND via particle self-assembly. Under centrifugation, DND self-ordered, and the effects of colloid formation on the refractive index and on light scattering within them were examined [24]. In addition, upon drying a DND suspension at various pH values and temperatures, DND particles self-assembled into one-dimensional fibers or two-dimensional thin films [25]; in that study, a band gap of 4.5 eV was shown to correlate with optical absorption. Nevertheless, the spectral properties of NDs' ordered systems remain generally poorly understood. In particular, the photoluminescence behavior of NDs following the formation of colored structures remains unexplored.

In this paper, we report and analyze the spectral properties of a colloidal-ordered structure composed of 100 nm NDs. A rainbow-colored colloidal structure of 100 nm ND was prepared, and the photoluminescence of its fragments transferred to a silicon (Si) substrate was observed at 488 nm wavelength laser excitation. The spectra were measured and discussed in terms of the formation of a structure similar to a colloidal photonic crystal with intrinsic luminescence.

2. Materials and Methods

2.1. ND Sample Preparation

The ND powders of polycrystalline particles with a nominal size of 100 nm were purchased from Kay Diamond Products (KDP, Boca Raton, FL, USA), produced using the HPHT method (Type KDM, Lot #17870) and subjected to strong acid pretreatment after the synthesis process.

The as-received ND was prepared to obtain a rainbow-colored colloidal structure by washing with strong acids using the method described in [26]. Briefly, the treatment consisted of a mixture of concentrated H_2SO_4 and HNO_3 (3:1 *v/v*) kept at room temperature for 24 h. The sample was then sequentially treated with 0.1 M NaOH and 0.1 M HCl aqueous solutions, and after each addition, the sample was heated at 90 °C for 2 h. The resulting product was thoroughly washed with deionized water, collected through centrifugation (Z323K, HERMLE, Wehingen, Germany), and dried. This treatment removes non-carbon impurities and non-diamond surface carbon while introducing oxygen-containing surface

groups (primarily carboxyl groups, $-\text{COOH}$), thereby yielding carboxylated nanodiamonds. To obtain a rainbow-like colloidal structure from NDs, we employed a method similar to that described in [22]. The procedure involved several centrifugation and washing steps, resulting in the ordering of nanodiamonds into a structure that appeared as a pattern of vertically separated multicolored layers within the centrifuge tubes (Figure 1a).

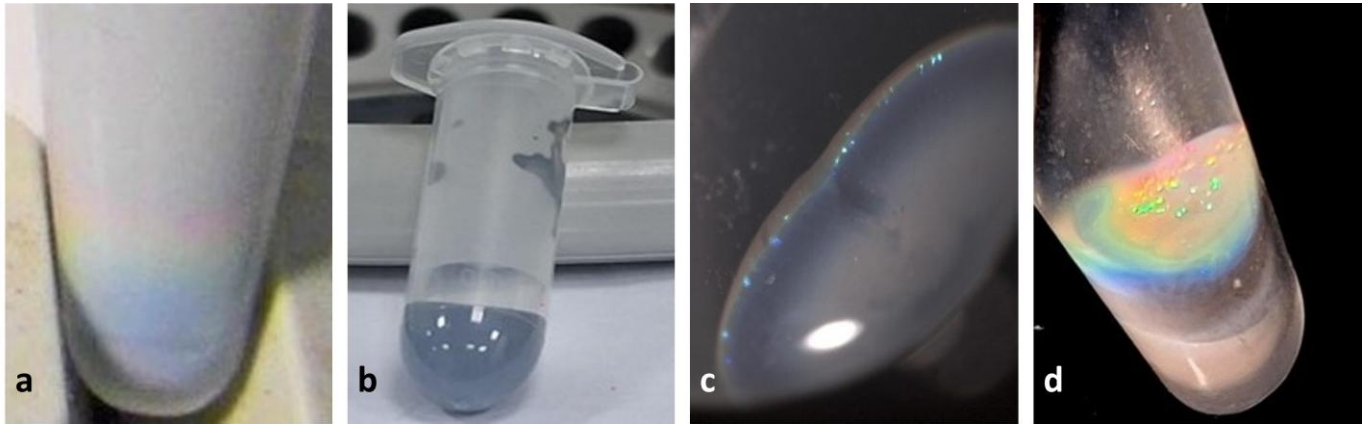


Figure 1. Steps for obtaining rainbow-colored layers in a centrifuge tube: (a) general view of the tube; (b) blue layer; (c) opalescent formations on the edge; (d) rainbow-colored structure with opalescent formations on the top layers.

The as-prepared ND powder was suspended in deionized water (Direct-Q 3 UV, Millipore, Molsheim, France) with concentration of 5 mg/mL. The suspension was poured into 1.5 mL microcentrifuge tubes, 1 mL in each (typically 12 to 24 tubes per experiment). They were then centrifuged for 15 min at approximately 8000–9000 relative centrifugal force (rcf) two to three times, with the supernatant replaced by fresh deionized water after each run. As a result, a relatively thick blue layer formed on top of the sediment. These upper blue layers from each centrifuge tube were collected and pooled together in a fresh microcentrifuge tube (Figure 1b). The collected suspension was diluted with deionized water to a final volume of ~1 mL and centrifuged repeatedly (3–5 times) for 15–30 min at 1000–2000 rcf. This resulted in the formation of a rainbow-colored layer within the tube (Figure 1a) with efficiency more than 90%. This entire procedure was done 10 times, with each time consistently yielding two tubes containing the rainbow-colored structure.

To obtain samples for microscopic observation and spectroscopic measurements, we attempted to carefully transfer a small aliquot of the suspension onto a substrate without disrupting the resulting structure, a task that proved to be exceptionally challenging. Si was used as a substrate, and the most successful approach involved using a small piece of a Si plate to gently scoop out a layer of the suspension, carefully avoiding any shaking, so that the selected area could remain intact and untouched.

More than 10 tubes containing rainbow-colored ND structure were used in attempts to transfer sample fragments onto Si substrates for spectral measurements. For each tube, only one—sometimes two—transfer attempts were possible, since the mechanical intervention inevitably disrupted the ordered arrangement. Finally, this resulted in six samples that retained the structure and were suitable for spectral and microscopic measurements.

Attempts to stabilize the sample for transfer, for example, by freezing or using auxiliary tools such as pipettes or capillaries, immediately resulted in the destruction of the rainbow-colored structure. Nevertheless, the ordered colloidal ND material, once transferred to Si, could be at least partially preserved even after drying. Spectral measurements were performed without waiting for the ND to dry completely on the Si substrate and could be continued after the sample had dried.

It should be noted that acid treatment was performed for the samples intended for spectral measurements, but the rainbow-colored colloidal structures with iridescence formations observed at the top/edges (Figure 1c,d) could also be obtained from the as-purchased nanoparticles. It was facilitated through additional mechanical treatment—such as shaking or low-energy sonication to promote better particle dispersion—and by optimizing the parameters of these treatments as well as the centrifugation conditions (duration, number of cycles, and rcf). Visual observations of the resulting ordered colloidal structures have shown that their coloring and iridescence remain stable for a certain period (tens of minutes) when left at rest.

2.2. Characterization of ND and Spectral Measurements

After acid treatment and after obtaining the colloidal organized structure, ND was characterized. Particle size and ζ -potential were estimated through dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, England, UK). The ND in aqueous suspension used in this study were characterized as having a number Z-average diameter (PDI 0.164) of 150–195 nm, with a ζ -potential at neutral pH ranging from −32 to −40 mV. The ND assembled from the blue layer, which provided the iridescent colloidal structure, had a number Z-average diameter of 160–180 nm (PDI 0.103) with a narrower size distribution and a highly negative ζ -potential of up to −50 mV. The DLS measurements were performed 10 times.

The formation of surface functional groups (in particular, −COOH) after the acid treatment procedure was confirmed by FTIR using an ABB Bomem MB154 FTIR spectrometer (Bomem, Quebec, QC, Canada). Specifically, the spectra exhibited characteristic absorption bands in the 1720–1780 cm^{-1} range (stretching of C=O of the carboxyl group) and 1630–1640 cm^{-1} (O–H bending), C–H groups with vibrations in the 2800–3000 cm^{-1} range, as well as a set of poorly resolved/overlapping peaks of other oxygen-containing groups in the 1000–1500 cm^{-1} range [26].

To prepare a control sample for spectral measurements, a drop of aqueous suspension of the acid-treated ND of concentration 5 mg/mL was applied to a Si substrate and dried. Photoluminescence spectra of the ND were recorded using an α -SNOM Raman microspectrometer (Witec, Ulm, Germany) with excitation from an Ar-ion laser (Melles-Griot, Carlsbad CA, USA) with a wavelength of 488 nm and a laser power of order 1 mW focused through a Nikon (Tokyo, Japan) CFI Plan Achrom NCG 100X NA 0.9 (WD 1.0 mm) objective, using a 150 grooves/mm diffraction grating. Spectral resolution of the spectrometer was 4 cm^{-1} . The acquisition time was of 10–20 s. The Raman spectra of the ND were also measured using a 600 grooves/mm diffraction grating. An intense narrow peak observed at 1332 cm^{-1} confirmed the predominant sp^3 hybridization of the ND, consistent with diamond crystallinity.

To investigate the emission spectra of the colloidal-ordered structures of ND, the samples prepared as described above were examined. The sample on the Si substrate was placed on the microscope stage under laser excitation. To select the area of interest of the sample, the stage was moved to locate both regions with observable emission comparable to that of the control sample and regions showing multicolored luminescence, which often exhibited increased intensity. For each of the four samples, 10–25 spectra were recorded at different points. Luminescence microscopy images of the structures were also acquired. Spectra processing was performed using the WITec Project software v. 3 (Witec GmbH, Ulm, Germany) and Origin 2018 (OriginLab Corp., Northampton, MA, USA).

Scanning electron microscopy (SEM) images were obtained from the completely dried samples using a JEOL JSM6500F SEM (JEOL, Akishima, Japan).

3. Results

Obtaining a colloidal organized structure of ND was initially evidenced by the appearance of rainbow-colored layers in a centrifuge tube. Within these layers—or on their top—opalescent formations visible under white light are also observable, even with the naked eye (Figure 1 c,d).

Spectra of the control ND sample (Figure 2a) and of the samples extracted from the upper layer of the structure shown in Figure 1 (Figure 2b) were measured. Figure 2a clearly shows that the spectra are a combination of a broad band characteristic of ND photoluminescence and Raman bands from both ND and the Si substrate. The luminescence spectra in Figure 2a vary slightly depending on the acquisition point and the control sample, but in general they are typical of as-prepared HPHT ND (in particular, ND with a predominant diamond crystal lattice). In this case, ND luminescence mainly originates from defects in the diamond lattice. Among the numerous diamond color centers, NV centers (NV^0 , NV^-), H4, H3, and several others can be excited at 488 nm and emit in the 490–750 nm range [6]. Furthermore, even after acid treatment, the surface of HPHT ND still contains disordered sp^2 - and sp^3 -hybridized carbon, which forms features with a narrower band gap than that of bulk diamond. Along with lattice defects, these surface inhomogeneities and recombination processes give rise to the observed photoluminescence of ND [7,9,10,27]. The shape and intensity of the spectra in different parts of the ND powder layer may vary to some extent (as the spectra in Figure 2a show). Narrow sharp peaks observed against the background of the luminescence signal can be attributed to Raman signals from ND and the Si substrate (Raman shifts at 521 cm^{-1} and $900\text{--}990\text{ cm}^{-1}$). The peak observed at $\sim 522\text{ nm}$ is the Raman band of ND, corresponding to a Raman shift of 1332 cm^{-1} , which characterizes sp^3 hybridization of carbon (diamond lattice).

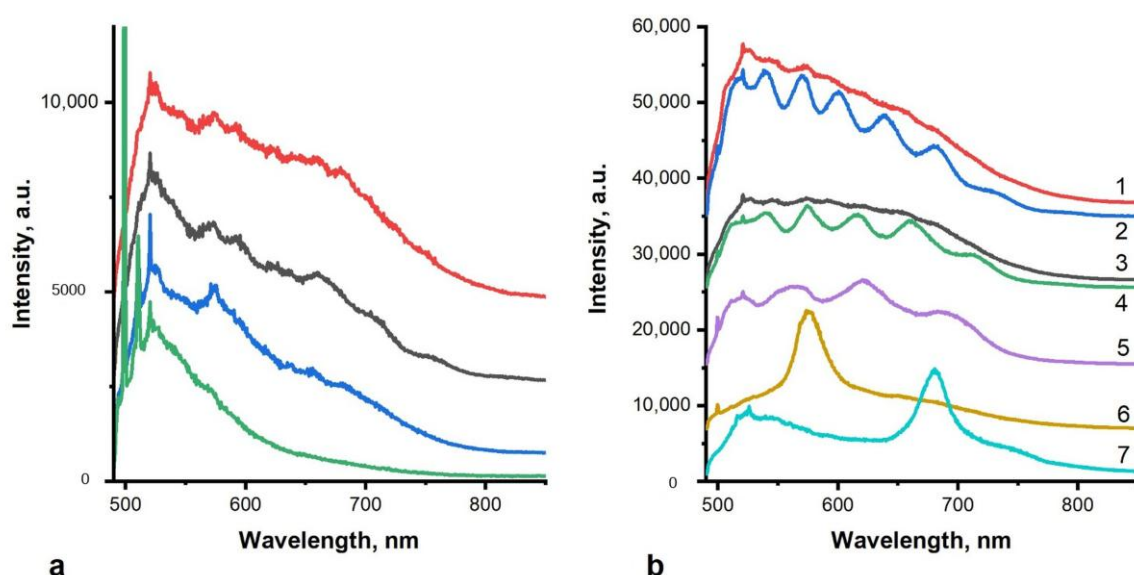


Figure 2. Luminescence spectra of nanodiamonds: (a) control ND; (b) colloidal-ordered ND structures transferred onto Si substrates. Spectra were measured using an α -SNOM microspectrometer with 488 nm wavelength laser excitation and a laser power of $\sim 1\text{ mW}$.

Some spectra obtained from the colloidal-ordered structures transferred to Si substrates can appear similar to the control spectra within the inherent spectral variability shown in Figure 2a (the examples of which are the spectra 1 and 3 in Figure 2b). However, these samples additionally exhibit a large number of bright emission areas, examples of which are spectra 2 and 4–7. Spectra of this type are characterized by higher intensity and

may display one or more relatively narrow lines or resemble an interference pattern. The spectra were measured on sample areas that showed emission with a predominance of a single specific color upon 488 nm wavelength laser excitation; representative examples of these spectra, along with the corresponding images, are presented in Figure 3 and its insets. Thus, we observe the typical HPHT ND luminescence (control spectra) from both acid-treated dry samples and those under the same conditions as the colloidal-ordered structure transferred on Si. Against this background, the spectra of luminescent areas are prominently visible and are found exclusively in the colloidal-ordered samples. The intensity ratio of the different types of spectra described above was evaluated, and it turned out that in areas exhibiting bright luminescence, the intensity can be at least to 6.5 times higher than in the control areas. Similar to the fact that the shape and intensity of the control spectra in Figure 2 vary, spectra measured in bright areas exhibit even more pronounced variations across different selected regions of the sample. Nevertheless, the emission is highly stable, and the spectra are well-reproducible when measured repeatedly at any given point. Representative results of this reproducibility assessment are provided in the Supplementary Materials (Figures S1 and S2).

In addition to the readily detectable luminescence in numerous small spot areas across the sample (Figures 2 and 3), a noticeable number of extended, structured luminescent regions (assemblies) was also observed. These areas exhibited bright luminescence upon laser excitation (Figures 4a and S3a); SEM micrographs of such kind of features are presented in Figures 4b and S3b.

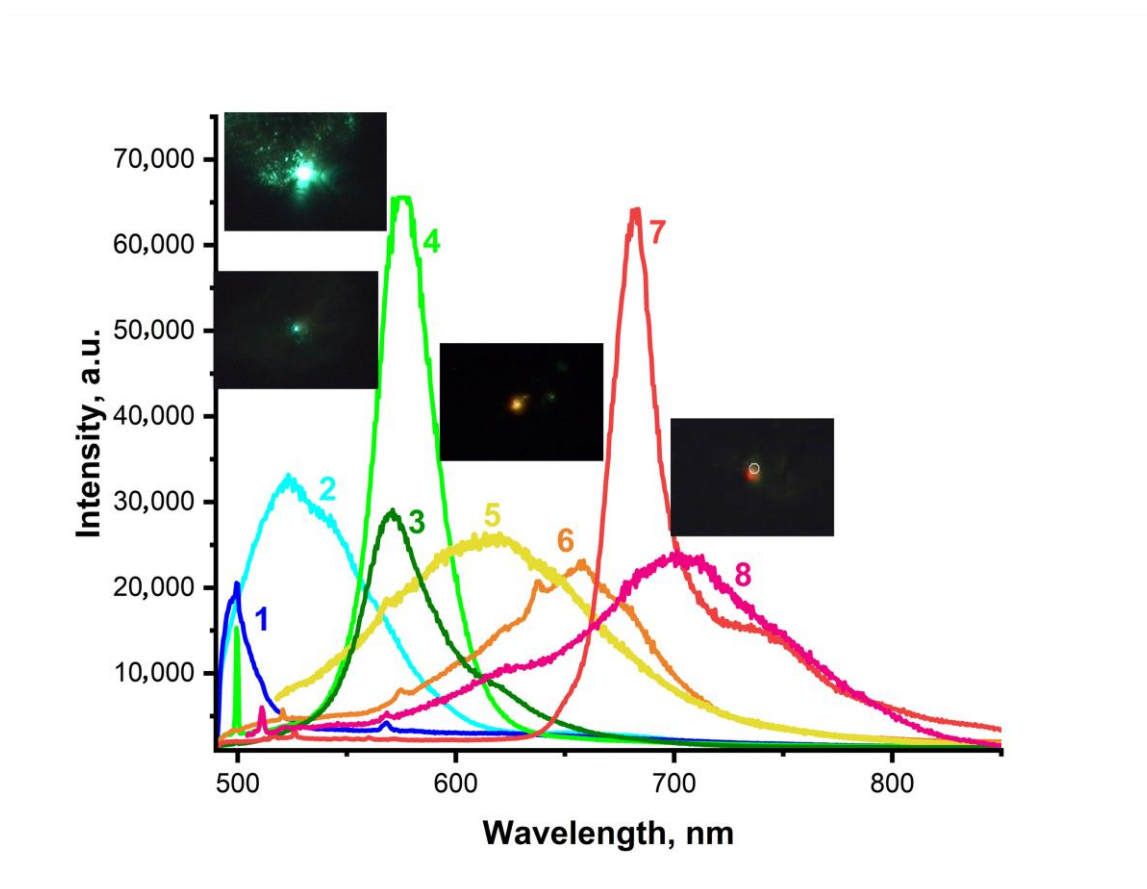


Figure 3. Examples of spectra measured in selected regions exhibiting bright emission of a predominant color. The insets show representative images observed under a microscope. Measured using an α -SNOM microspectrometer at 488 nm wavelength laser excitation with a laser power of ~1 mW.

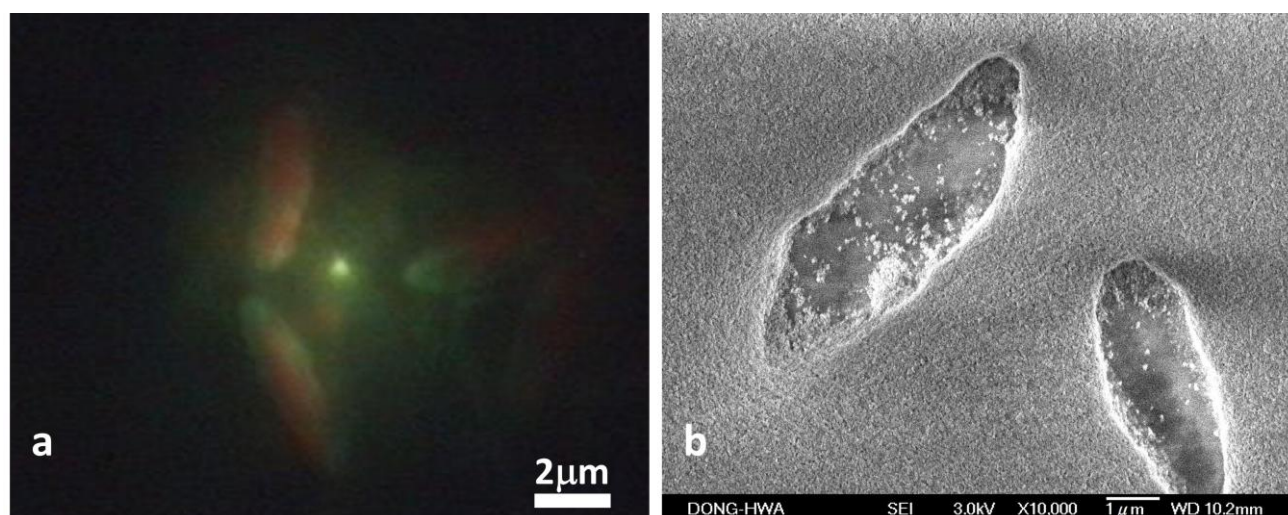


Figure 4. Luminescence image obtained using an α -SNOM microspectrometer (a) and SEM image obtained with a JEOL JSM6500F scanning electron microscope (b) of the formations in a sample of colloidally ordered ND structure transferred onto a Si substrate.

4. Discussion

The presented results confirmed that such complex materials as ND, despite being inherently heterogeneous in size, shape, surface chemistry, and particle crystallinity, are nevertheless capable of forming regular structures under certain conditions. The colloidally ordered structure is initially identified at the macroscopic level through the formation of rainbow layers; and the ordering of ND particles into micrometer-sized structures is observed under white light illumination (Figure 1c,d) via their opalescence. When excited with a 488 nm wavelength laser, it is detected through luminescence emission (Figures 4a and S3a) and also by SEM imaging of dried samples (Figures 4b and S3b). Figure 4a demonstrates also characteristic glow from the ND outside the luminescent area at the focus of the microscope objective under laser excitation.

Previous studies have considered the ordering of ND particles in colloids exhibiting photonic crystal properties and have proposed several conditions for this ordering. In particular, it has been suggested that the formation of ND colloidal photonic crystals requires a high absolute value of surface potential that is non-uniformly distributed over the particle surface due to the presence of different functional groups [23]. In our case, the high ζ -potential (reaching -50 mV) measured for the centrifuged ND samples, along with the variety of surface functional groups identified through FTIR spectroscopy, are generally consistent with these requirements. Beyond these general requirements, the specific mechanism of colloidal ordering has been discussed in the literature. Regarding the colloidal structure of ND, it was suggested [22] that it is largely governed by a gradual change in interparticle distance, driven by the gradient of centrifugal forces along the tube during centrifugation. In contrast, there was proposed that the size gradient arises not from a change in interparticle spacing, but from the distribution of particles according to their size; consequently, light scattering by layers of differently sized particles gives rise to rainbow coloration [28]. Notably, both above-mentioned studies discuss only scattering (based on refraction properties) considering the formed structure as a photonic-crystal-like. However, due to the luminescence properties of NDs, the formed colloidal-ordered structure should be regarded not merely as a photonic crystal, but rather as a luminescent photonic crystal, or, more precisely, as a colloidal photonic crystal with intrinsic luminescence. Such systems attract considerable interest owing to the research and practical opportunities offered by combining reflected/scattered light from photonic crystals with their intrinsic emission [29]. From a practical standpoint, this interest stems from their

responsiveness to external stimuli (promising as colorimetric indicator platform for sensing and detection applications) and to the internal ones, such as structural changes, which can be exploited for optical tuning [29,30]. Finally, the fabrication of colloidal luminescent photonic crystals is itself a topic of active research [30]. However, this approach is generally considered to impose stringent constraints on particle size and shape, or to require high monodispersity. Moreover, the preparation of such systems often involves the incorporation of luminophores exhibiting aggregation-induced emission (AIE) to circumvent the issue of aggregation-caused quenching [29,31].

Although NDs generally lack the shape homogeneity and size monodispersity typically required for photonic crystals, the luminescence spectra of samples derived from colloidally ordered NDs (Figures 2b and 3) reveal features indicative of an ordered structure and suggest photonic-crystal-like behavior. Control spectra in Figure 2a,b (spectra 1 and 3, measured outside the bright-emitting regions), show a broad band characteristic of HPHT ND and are largely similar to one another. In contrast, the spectra acquired from the brightly emitting areas of the ordered sample (Figures 2b and 3) exhibit narrow individual emission bands, whose peak wavelengths match the colors observed in the microscopic images, and also display interference features. Comparison of spectra 1 vs. 2, 3 vs. 4 (Figure 2b) and the full set of spectra 1–3, 5, 6, and 8 (Figure 3) with spectra 1 and 3 (Figure 2b) shows that both the interference-type spectra and the distinct isolated peaks fall within the luminescence spectral range of ND. Depending on the localization of the focused excitation light on the sample, it is evident that we obtained intensity-modulated emission from nearly the entire possible area of luminescence of the ND (spectra 2, 4, 5 in Figure 2b). When the excitation was focused on thicker colloidally ordered structures, a narrowed luminescence band emerged, still within the same overall ND luminescence range (spectra 6 and 7 in Figures 2b; and 3). Based on the obtained spectra, and taking into account that the refractive index of ND is considered to lie in the range of 2.41–2.68 [24], the thickness of the ordered layers is estimated to be 1–3.5 μm using the free spectral range (FSR) equation; the examples of estimations are presented in Figure S4a,b. A more precise dimensions could be clarified with a better-defined refractive index for the system. Thus, such a system can also serve as a model for addressing the inverse problem of determining the refractive index of ND in a two-component system, provided that the spectral data are complemented by reliable geometric information on the colloidally ordered structure (e.g., from SEM), a topic that has received considerable attention [32]. Observation of luminescent formations in the fragment of the colloidal-ordered ND structure is correlated with the presence of formations of similar dimensions in SEM images (Figures 4 and S3b). In further studies, analysis of such images will be useful for understanding the structure of the ND system under investigation and for developing methods to obtain stable ordered ND systems, both for fundamental research and for potential applications.

The fact that the resulting structures proved to be sufficiently stable upon drying allowed us to focus specifically on their spectral properties. However, since the system involves the ordering of ND in a colloidal structure, it is important to further investigate the spectral features in the colloidal state, their relation with the structure, the behavior upon structural changes (including drying), and the interaction with the solvent. Despite the fact that these aspects still remain unclear, it should be noted that the formation of colloidal luminescent photonic crystals and ability to modulate emission over a broad spectral range attracts great interest. For instance, one can envisage future applications in which modulation is achieved by tuning the crystal conformation in response to changes in water concentration [29]. Furthermore, such colloidal ND structures are promising for fabricating systems with micrometer-scale characteristic dimensions. The production and characterization of colloidally ordered systems from ND of different sizes and structures,

along with the study of the emission properties arising from the interplay of ND luminescence and light scattering/refraction by the ordered particles, open up additional opportunities, both for fundamental research (particularly on optical-spectral and colloidal properties) and for the development of novel ND-based materials for further applications.

Beyond the luminescence properties of ND suspensions arising from the synergy between colloidal ordering and ND emission, we would like to propose that another mechanism, namely, aggregation-induced emission (AIE) may also play a role. When relatively stable colloiddally ordered structures are formed and maintained over time, centrifugation could create conditions favoring close interactions between particle surfaces, which is a prerequisite for AIE [33]. In the context of nanoparticle aggregation, the cluster-triggered emission (CTE) mechanism is most often invoked [34]. This model is based on the idea that the large bandgap of a non-luminescent material narrows due to newly formed through-space conjugation (electron coupling), such as $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, or $\pi \rightarrow \pi^*$ interactions, as well as hydrogen bonding, all driven by electron delocalization. Such conjugation can indeed occur on ND surfaces. For example, $n(\text{OH}) \rightarrow \pi^*(\text{CO})$ conjugation on the ND surface has been reported to influence luminescence, causing a red shift in emission originating from surface features [10]. Hydrogen bonding both on and between ND surfaces of varying sizes and origins, affecting IR absorption properties, has also been discussed [26]. Moreover, AIE has been observed and its mechanisms explored for carbon dots (CDs) [35], whose surface structure, featuring non-diamond carbon (sp^2/sp^3) and a similar set of functional groups, is comparable to that of ND. This parallel allows us to consider both the contribution of carbon-dot-like luminescence in ND [14] and the potential role of the surface in creating conditions conducive to AIE/CTE [36]. While this idea is speculative and demands further study, it reinforces the potential of ND for luminescent photonic crystals.

5. Conclusions

ND produced by the HPHT method are generally considered practically unsuitable for forming ordered colloidal structures due to their inherent polydispersity and irregular shape. Nevertheless, it was shown that suspensions of DND and HPHT ND with a particle size of about 100 nm can organize into colloiddally ordered structures with observed noteworthy and intriguing light-scattering properties, thus, its photonic-crystal-like structure has been discussed [22,23]. However, although nanodiamonds possess intrinsic photoluminescence that should significantly influence the interaction of the colloidal ND structure with excitation light, to the best of our knowledge, the spectral properties of such structures have not been previously investigated.

In this work, we observe and discuss the spectral properties of the ND colloid-ordered structure. Under centrifugation-induced sedimentation, HPHT 100 nm ND form rainbow-colored layers in the centrifuge tube. Fragments of the top layer of the rainbow-colored structures were transferred onto a Si substrate for spectroscopic measurements. Upon 488 nm wavelength laser excitation, multicolor luminescence could be observed from specific regions of the sample. The recorded spectra revealed distinct features arising from the ordering of diamond nanoparticles into a structure capable of modulating ND-emitted luminescence. The characteristic dimension of such structures was approximately estimated.

Despite its sensitivity to external factors (mechanical and thermal), the system formed upon the ordering of NDs was observed stable upon drying. This allowed us to focus specifically on their spectral properties. Our findings thus demonstrate the feasibility of fabricating photonic-crystal-like structures with intrinsic luminescence from irregular nanoparticles and open up new opportunities for studying NDs' optical properties and for advancing photonic applications. At the same time, since the ordering of NDs occurs

within a colloidal framework, it is essential to extend the investigation to the spectral features in the colloidal state, their structural dependence, the evolution upon structural changes (such as drying), and the role of solvent interactions. Understanding these aspects in turn highlights the potential for practical applications of these structures. Thus, in particular, they could find use in optoelectronics as controllable tunable sources emitters; as colorimetric indicator platform in sensing and visual detection; and, given the biocompatibility of ND, in biosensing, in the development of labels and “smart” inks, etc. They can also serve as a model system for fundamental studies of light–matter interaction, including with nanomaterials, and for investigating the influence of a periodic dielectric structure on the spontaneous emission of color centers.

However, to unambiguously establish the photonic crystal nature of the observed structures, dedicated follow-up studies are required to confirm the mechanism underlying the observed luminescence modification. These investigations, which now lie beyond the scope of the present work, constitute a necessary next step toward the full characterization and exploitation of these novel ND-based photonic materials.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/c12030063/s1>, Figure S1: Estimation of temporal reproducibility of the spectra measured in the same point (close location) are analyzed; Figure S2: Spectra are measured in different (close) points of every selected area; Figure S3: Luminescence (a) and SEM (b) images of the formations in a sample of colloiddally ordered ND structure transferred onto a Si substrate. ; Figure S4: Examples of estimation of characteristic dimensions of ND ordering using FSR equation, using Origin.;

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Abbreviations

The following abbreviations are used in this manuscript:

ND	Nanodiamond
DND	Detonation nanodiamond
HPHT	High-pressure high-temperature
FTIR	Fourier transformed infrared
SEM	Scanning electron microscope
AIE	Aggregation-induced emission
CTE	Cluster-triggered emission
rcf	Relative centrifugal force
FCR	Free spectral range

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