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(54) Title: WIDE BAND GAP SEMICONDUCTOR OPTIMIZATION FOR HYPERPOLARIZATION

(57) Abstract: A method of hyperpolarizing one of either a diamond or silicon carbide material includes annealing particles of the material for a time period in the range of 1 to 60 minutes at a temperature in the range of 1300 - 2000 degrees Celsius to produce annealed particles, selecting ones of the annealed particles having a nitrogen vacancy in the range of 1 to 15 parts per million, illuminating the selected particles with laser light, and subjecting the selected particles to one of either microwave radiation or magnetic field sweeps to produce hyperpolarized particles.

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WIDE BAND GAP SEMICONDUCTOR OPTIMIZATION FOR HYPERPOLARIZATION

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to and the benefit of US Provisional Application No. 62/847,677 filed May 14, 2019, which is incorporated herein by reference in its entirety.

GOVERNMENT RIGHTS

[0002] This invention was made with government support under Grant Number R43CA232901, awarded by National Cancer Institute of the National Institute of Health. The government has certain rights in this invention.

TECHNICAL FIELD

[0003] This disclosure relates to hyperpolarization of wide band gap semiconductor particles, more particularly to optimization of hyperpolarized wide band gap semiconductor.

BACKGROUND

[0004] Defect centers in wide bandgap semiconductor materials, for instance diamond and silicon carbide, have attracted immense attention for their enabling role in several quantum technologies. This has been driven by a combination of their attractive spin and optical properties – optical initialization and readout electronic spin qubit states, long spin coherence times even at room temperature, and the ability to engineer defect centers on-demand at relatively high densities. Indeed, a new era of optical quantum sensing platforms have been ushered in by these materials, enabling construction of ultrasensitive solid-state sensors of magnetic, electric fields and temperature.

[0005] Particulate forms of these “quantum materials” additionally open a plethora of other attractive applications stemming from their small size and high surface area. For instance nanodiamond (ND) particles can be deployed as targetable “in cell” quantum sensors for

magnetic fields and temperature. Following exciting recent developments, nanodiamonds have also emerged as a new paradigm for optical hyperpolarization that promises to upturn and vastly enhance classical nuclear magnetic resonance spectroscopy (NMR) and imaging (MRI). This relies on the fact that the nitrogen vacancy (NV) centers in these diamond particles (in the NV⁻ charge state) can be optically polarized close to 100% even at room temperature and independent of magnetic field. This vastly athermal spin polarization can then be potentially transferred to nuclear spins (of an external liquid for instance) in contact with the high surface area particles, hyperpolarizing them through Overhauser means, and enhancing their NMR signature by orders of magnitude. A method of optical ¹³C hyperpolarization in diamond particles has been developed, showing their efficient polarization at low fields (1-70mT), and high throughput $\geq 20\text{mg/min}$, and demonstrated the ability to construct low cost diamond hyperpolarizer devices that could retrofit existing NMR and MRI magnet systems. Large (200 μm) diamond microparticles had their ¹³C nuclei optically hyperpolarized $\approx 0.75\%$ level, a gain over their Boltzmann polarization at high field (7T) by about a factor of 750, and corresponding to a time acceleration of imaging these particles in MRI by over million-fold (A. Ajoy, K. Liu, R. Nazaryan, X. Lv, P. R. Zangara, B. Safvati, G. Wang, D. Arnold, G. Li, A. Lin, et al., Sci. Adv. 4, eaar5492 (2018)).

[0006] Indeed, optical methods for dynamic nuclear polarization (DNP) present several advantages over conventional methods involving cryogenic temperatures and large magnetic fields. Hyperpolarization can be generated replenishably and under ambient conditions with no NV quenching. If relayed from the ¹³C nuclei in diamond lattice to chemical groups and molecular species on diamond surfaces or into a surrounding liquid, this would allow for the injection of hyperpolarized reactants to illuminate materials, catalysts, and reaction mechanisms constrained to material surfaces, and generally new modalities for ultrafast MR

spectroscopy and imaging. Hyperpolarization in diamond particles also opens the exciting possibility of “dual-mode” optical and MRI imaging. Since NV-rich nanodiamonds fluoresce brightly, are non-toxic, and can be surface functionalized, they have been widely used as non-blinking optical biomarkers, especially for tumor detection. However given finite optical penetration depths, the fluorescence is exponentially attenuated making them hard to discern in tissue beyond a depth of ~1 cm. Hyperpolarization however renders the particles “MRI bright” with no depth limit. The images are susceptible to different other sources of noise (RF/magnetic as opposed to optical), and the polarization survives for long periods often in excess of 10 min. Colocalizing the optical and MRI images in the same system can vastly increase the overall image SNR, and enable new directions for in-situ biological imaging.

[0007] While there has been tremendous progress in optimizing diamond particles for fluorescence, including in diamond growth, milling and annealing conditions, and defect incorporation by electron irradiation, a detailed materials science study is critical to produce best particles for hyperpolarization. Apriori it is not completely clear that the same conditions that produce the optically brightest particles are even the same as those that make them maximally MRI bright. Hyperpolarization buildup is strongly contingent on NV electron spin coherence (T_{2e}) times and nuclear relaxation (T_{1n}) lifetimes, which are determined in large part by paramagnetic impurities and lattice distortions, conditions that are relatively less stringent for optical brightness.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figures 1A-1D show graphs of results and photographs of an embodiment of a diamond hyperpolarization process using room temperature optical pumping.

[0009] Figures 2A-2E show graphs of results of an embodiment of a diamond hyperpolarization process with different nitrogen vacancy center concentrations under different irradiation doses.

[0010] Figure 3A-3C show graphs of results of an embodiment of a diamond hyperpolarization process across different particle sizes.

[0011] Figures 4A-4E show graphs of results and photographs of an embodiment of a diamond hyperpolarization process under rapid thermal annealing conditions.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0012] The embodiment here identify conditions for the construction of wide band gap semiconductor particles that make an “optimal” particle for nuclear hyperpolarization. The below discussion focuses on diamond particles based on experiment using them, but no limitation to such particles is intended, nor should any such limitation be implied. These embodiments could also apply to wide band-gap semiconductors including diamonds, silicon carbide, etc.

[0013] As used below, the term “nitrogen vacancy” or NV means a nitrogen vacancy center, a center consisting of a vacancy and a nitrogen atom. A vacancy is a lattice site with an absent atom in materials such as diamonds and silicon carbide. Other wide band-gap materials may have similar creation defects, where a creation defect results in an electron spin and the material has a nuclei spin. The electron spins can be hyperpolarized and the hyperpolarization can be transferred to the nuclei.

[0014] The embodiments undertake the first such systematic study comparing hyperpolarization in diamond particles across different material dimensions – particle size, NV concentration and annealing conditions. The embodiments focus on high-pressure, high-temperature (HPHT) diamond particles (J.-P. Boudou, P. A. Curmi, F. Jelezko, J. Wrachtrup,

P. Aubert, M. Sennour, G. Balasubramanian, R. Reuter, A. Thorel, and E. Gaffet, Nanotechnology 20, 235602 (2009) “Ajoy I”), since given their ease of production at scale, they would likely form the basis of any hyperpolarization technology based on diamond. However, diamond particles produced by other synthesis methods, such as for example, using chemical vapor deposition method, harvesting naturally occurring particles, or produced by other known methods in the field can be also candidates for hyperpolarization technology. Particles can have natural abundance ^{13}C or can be enriched with ^{13}C . It has been observed counterintuitively that high NV center concentrations have a deleterious effect on the hyperpolarization enhancements, and rapid high temperature annealing (RTA) recipes can relieve strain and paramagnetic impurities in the diamond lattice for vastly enhanced hyperpolarization performance. As a result, particles have been obtained that have the best (size-normalized) hyperpolarization efficiency reported in the literature for $15\mu\text{m}$ microparticles. This work hence paves the way for the guided materials production of highly “hyperpolarizable” diamond particles.

[0015] Experiments are performed on HPHT particle samples comparing their performance for room temperature DNP under optimal conditions. Initially, the particles are irradiated with electron radiation, and then annealed in either a ‘standard’ or a high temperature (HTA) annealing process. The particles (all at natural abundance ^{13}C) are illuminated with 520 nm laser light to polarize the NV electrons at low field $B_{pol}=38\text{mT}$, and subjected to “chirped,” or pulsed, microwave (MW) irradiation over the NV ESR spectrum in order to excite hyperpolarization to the ^{13}C nuclei (see Fig. 1) (Ajoy I). The microwaves may be applied in a ramped fashion. Alternatively, the microwaves may be selected tailored to the electronic spectrum used. The swept MWs excite a sequence of Landau-Zener transitions in the rotating frame that causes a coherent transfer of polarization (Ajoy I and P. R. Zangara, S. Dhomkar,

A. Ajoy, K. Liu, R. Nazaryan, D. Pagliero, D. Suter, J. A. Reimer, A. Pines, and C. A. Meriles, Proceedings of the National Academy of Sciences, 201811994 (2019)). The particles may also be subjected to magnetic field sweeps.

[0016] The process estimates a polarization transfer efficiency per sweep event $>10\%$, and in practice the process increases the HP efficiency by using multiple cascaded sweepers forming a MW frequency comb (A. Ajoy, R. Nazaryan, K. Liu, X. Lv, B. Safvati, G. Wang, E. Druga, J. Reimer, D. Suter, C. Ramanathan, et al., Proceedings of the National Academy of Sciences 115, 10576 (2018)). The ^{13}C NMR signature of these particles are measured at 7T by rapid sample shuttling, the travel period ($<700\text{ms}$) being negligible in proportion to $T_{1\rho}$.

[0017] Figure 1A shows typical hyperpolarization results. The line 10 shows the dynamic nuclear polarization (DNP), a 7T thermal signal, zoomed in the line 12 in the inset. The ratio of signals allows the estimation of the hyperpolarization enhancement factor ϵ with respect to 7T. Figure 1B shows the DNP buildup curve under typical conditions. The curve 14 shows the buildup of hyperpolarization under optical pumping. Figure 1C shows one embodiment of a combination of laser illumination and microwave irradiation. In this embodiment, the laser illumination occurs as 520 nanometers (nm) with a power of 80 milliWatts/millimeter square (mW/mm^2). As will be discussed in more detail further, this process occurs in the presence of a magnetic field. For hyperpolarization, the magnetic field is 40 mT or less, but may be in the range of 0.1 T to 1 T, referred to here as a low field. High field, as used here, means a field of 7T.

[0018] Figure 1D shows a of a laser fixture 20 delivering optical radiation through an octagonal ring 22 of multimode optical fibers ($\sim 800\text{ mW}$) such as 24, approximating a toroidal irradiation pattern. An additional laser is applied from the bottom 26. Beam diameters are $\approx 4\text{ mm}$ at point of contact with the diamond particle sample, which is carried

in a test tube and under water. The chamber 22 may contain a Helmholtz coil 28, shown in Figure 1E.

[0019] The hyperpolarization in a large mass (20 mg) can be studied by plotting a polar representation of the effects of irradiating the sample with various nearest-neighbor (NN) only combinations of an increasing number of lasers arranged on the octagonal ring. One can observe an approximately circular buildup of homogeneous buildup of polarization in the sample, with a slight deviation from circularity in the polar distribution arising from experimental imperfections, primarily microwave inhomogeneity. Sub-linear growth arises from the overlap of the NN laser beams, and saturation indicates that the polarization builds up uniformly over the entire 20 mg sample mass.

[0020] For a fair comparison between the various samples, their signals are mass normalized, and the polarization benchmarked against the unit mass thermal (Boltzmann) NMR signal obtained at 7T. These 7T DNP enhancement factors, henceforth labelled ϵ , which correspond to absolute polarization levels $\approx 0.1\epsilon\%$. Hyperpolarization builds up rapidly and saturates in under 90 seconds of optical pumping. For each of the samples, the embodiments determine polarization buildup and decay curves (under dark conditions), allowing quantification of the rates of NV induced polarization injection and rates of the inherent ^{13}C relaxation, allowing unique insight into the material conditions that determine them.

[0021] In order to ensure the entire mass (5-30mg) of the diamond particles is polarized, the process employs a laser excitation geometry where nine 800mW fiber coupled lasers are arranged along an octagonal ring. This provides a close approximation to a spherical laser excitation pattern to maximally penetrate all diamond particle surfaces. In a polar plot representation, Figs. 1A-D shows the obtained hyperpolarization enhancements using varying number of lasers, and for simplicity considering only nearest-neighbor (NN) combinations. A

spatially homogeneous buildup of polarization in the sample was found, to a good approximation. Plotting signal intensity averaged over all the number of lasers, one finds a sub-linear dependence (due to overlap of the NN beams) that saturates for masses $\leq 20\text{mg}$, demonstrating that the process indeed excites DNP optimally over the entire sample mass.

[0022] In Figs. 2A-E, one can study the saturation DNP enhancements with varying NV center concentration, produced by varying doses of electron irradiation. One should note that the particles are all of identical size (18 μm), and have been annealed after the electron irradiation under standard conditions that optimize particle brightness (850 $^{\circ}\text{C}$, 2 hours), allowing the process to separate individually the effect of increasing defect concentration. Substitutional nitrogen concentration in the starting particles was about 110 ppm according to EPR. Electron irradiation fluences varied in the experiments between $1 \times 10^{18} \text{ e/cm}^2$ to $5 \times 10^{19} \text{ e/cm}^2$ and electron beam energies varied between 1 MeV and 3 MeV.

[0023] Figure 2A shows the mass normalized hyperpolarization enhancements ϵ that indicate the DNP efficiency decreases at high NV concentrations. Comparisons with the optical fluorescence indicates that optimal NV concentrations for particle brightness and DNP differ. The line 30 shows mass normalized polarization enhancements for 18 micrometer particles at approximately 38 mT. The upper axis shows the corresponding NV^- concentrations. The line 32 shows the optical fluorescence and displays a similar trend. The inset shows the polarization buildup with line 34 and the decay with line 36.

[0024] Published ESR spectra for samples at different NV concentrations demonstrated the formation of satellite paramagnetic lattice defects at high NV concentration produced at high irradiation doses (A. I. Shames, A. I. Smirnov, S. Milikisiyants, E. O. Danilov, N. Nunn, G. McGuire, M. D. Torelli, and O. Shenderova, The Journal of Physical Chemistry C 121,

22335 (2017)). Figures 2B and 2C show polarization decay rates for the sample of Figures 2A, with Figure 2C showing the decay rates for high and low electron dose samples. Figure 2D shows a polarization injection rate from the buildup curves, and Figure 2E shows the polarization buildup from the samples in Figure 2B.

[0025] Results indicate that the injection rate increases with NV concentrations due to larger number of polarization sources in the lattice, but this comes with a concomitant deleterious cost of rapid decrease in spin relaxation lifetimes. As discussed below, these effects occur on both the polarization injection and decay rates from the high electron fluences leading to reduced hyperpolarization efficiency.

[0026] The discussion here focuses almost completely on diamond particles that are identically milled to a uniform size of $18 \pm 3 \mu\text{m}$, all starting from the same parent material. Fig. 2 shows data for samples prepared under varying fluences of electron irradiation and *standard* annealing conditions (850°C for 2 hrs), both of which can be precisely controlled. The increasing fluence results in an increasing NV⁻ center concentration that should seed a greater polarization in the ¹³C lattice. Practically, however, this is associated with concomitant lattice damage, as well as an increased paramagnetic defect concentration, resulting in a decrease in ¹³C T_1 times, and manifests as an inherent tradeoff in the hyperpolarization levels with fluence. This is evident in the experiments in Fig. 2A where one can observe a DNP optimum at $\approx 5 \times 10^{18} \text{ e/cm}^2$, estimated from EPR data to correspond to an NV⁻ concentration of $\sim 4\text{ppm}$ (upper axis). Furthermore, the DNP enhancements correlate with the optical brightness of the particles as shown in line 10 Fig. 2A, which also decreases at higher fluences, here due to the generation of paramagnetic optical traps.

[0027] The presence of paramagnetic spins bottlenecks hyperpolarization buildup in the high e-fluence samples. Indeed, the saturation hyperpolarization values reflect a dynamic

equilibrium between NV^- -induced polarization injection into the lattice ^{13}C nuclei, and its inherent decay due to nuclear T_1 processes. If β_i and β_d denote the (assumed monoexponential) polarization injection and decay rates respectively, the inset buildup curve of Fig. 2A has the functional form, $\varepsilon(t) = \beta_i/(\beta_i + \beta_d)[1 - e^{-(\beta_i + \beta_d)t}]$

[0028] For each sample, measurement of the polarization buildup and decay curves allows an independent estimation of injection and decay rates. Both parameters provide valuable insight into the material conditions that affect hyperpolarization levels; if for instance β_d is large, polarization saturates at a low value in spite of high NV^- concentrations. The buildup and decay curves are generally weakly bi-exponential, such as in Fig. 2A, because of disparate behavior between directly NV^- coupled ^{13}C and weaker bulk nuclei. One can, to a good approximation, quantify the buildup and decay rate constants and error bars through the inverse $(1 - 1/e)$ and $1/e$ intercepts of the fitted lines, respectively, depicted as buildup time and decay time in Fig. 2A.

[0029] The extracted ^{13}C relaxation rates grow steeply for the high e-fluence samples as in Fig. 2B, and as the representative decay curves from low and high fluence samples in Fig. 2C indicate, the differential in T_1 values can be as large as 5 times. One should note that the nuclear T_1 (spin-lattice) relaxation here is not phonon mediated; instead, at the operational hyperpolarization fields, it originates predominantly from stochastic spin-flipping noise produced at ^{13}C sites from lattice paramagnetic electrons. This mechanism is dominant since the nuclear Larmor frequency, $\omega_L = \gamma_n B_{\text{pol}}$ (for instance ≈ 380 kHz at 38mT) can lie within the dipolar-broadened EPR linewidth. The steep increase in relaxation rate in Fig. 2B therefore reflects the deleterious increase in paramagnetic content on the ^{13}C nuclei.

[0030] Similarly, looking at the extracted polarization injection rates of Fig. 2D, one can observe a saturation and decrease with increasing electron fluence. This is somewhat counterintuitive, since an increase in NV⁻ concentration should result in a greater number of sources seeding polarization into the ¹³C lattice. However the NV-¹³C polarization transfer is a coherent process, and Fig. 2D strongly suggests that the transfer efficiency per MW sweep event is decreased in the higher fluence samples. This is potentially due to the reduction in NV⁻ center coherence time T_{2e} from interactions with the surrounding para-magnetic spin bath, as well as charge noise from lattice ionic nitrogen species. Fig. 2 therefore illustrates that while one would like to electron irradiate samples to maximize the number of NV⁻ centers, this comes at a steep cost of lattice damage and para-magnetic impurity content, and strongly countervails against ¹³C hyperpolarization buildup.

[0031] The discussion now considers Figs. 3A-C and the dependence on particle size, employing particles starting from the same parent material that have been milled and fractionated to sizes as low as 100 nm. Hyperpolarization in small particles is important both for applications employing them as agents for optical DNP of external liquids, as well as for MRI imaging of the particles themselves. This is because of their increasing surface area to volume ratio that scales linearly with decreasing particle size, and the fact that small NDs can be safely injected into in vivo target disease locations. Indeed, the surface area of 100nm particles is comparable to conventional catalysts (7 m²/g), and when brought in contact with pyruvic acid, one can estimate reliable ¹³C polarization at a throughput of 1mmol/min.

[0032] In Figures 3A-3C, the DNP dependence on particle size was studied for samples that have been milled and fractionated from the same starting material. NV concentrations in all samples was approximately 3-4 ppm. Figure 3B shows a decrease in mass weighted hyperpolarization enhancements with size. Figure 3C shows surface area to volume

normalized results demonstrating that the 100 nm particles show best overall performance, making them candidates for polarization of external liquids. Sizes may range from 5 nm to 1000 microns, 10 nm to 100 microns, 100 nm to 18 microns.

[0033] Figure 3A shows decay curves at B_{pol} approximately equal to 38 mT that reveal that ^{13}C lifetimes are approximately independent of particle size down to 100 nm. The 3 μm sample has an exceptionally long ^{13}C lifetime since a lower electronic radiation irradiation dose and electron beam energy was employed in the sample.

[0034] The process has found the DNP enhancements decreasing with particle size, as shown in Figs. 3A-3C, which may arise from the increased role of surface effects at smaller particle sizes, especially with regards to maintaining the fine balance between NV^-/NV^0 concentrations under optical pumping. Fig. 3A shows the polarization decay rates at 38 mT and indicates the hyperpolarization decay is seemingly independent of particle size down to 100 nm. Fig. 3B shows representative mass normalized ^{13}C hyperpolarized spectra obtained from particles of varying size. Fig. 3C shows mass normalized polarization enhancements over 7T in line 40 having a steep decrease in DNP efficiency with particle size. When the data is normalized with respect to surface area-to-volume ratio shown as line 42, the smaller particles down to 100 nm show the best overall hyperpolarization levels per number of surface ^{13}C nuclei.

[0035] Therefore, when normalized by the surface area to volume ratio however, the 100nm ND sample does provide the best overall hyperpolarization efficiency as an agent for external polarization. External polarization involves transferring the hyperpolarization to external molecular nuclei external to nanodiamond particles, such as in a liquid containing the hyperpolarized particles.

[0036] Moreover, no direct correlation in the spin relaxation lifetimes with size at least down to 100 nm was observed. The enhanced $T_{1\rho}$ lifetime of the 3 μ m particles in Fig. 3 were because although the same electron fluence was used in all samples, this sample had a lower electron beam energy (1MeV in contrast to 2-3MeV in all other samples). This substantiates the notion that lattice damage arising from electron irradiation plays an important role in creating paramagnetic lattice defects and ultimately setting the nuclear relaxation times. It implies that employing low energy long time electron irradiation will allow for longer polarization buildups and larger associated gains in saturation DNP enhancements.

[0037] Finally, and perhaps most importantly, in Figs. 4A-4E, the discussion studies the DNP enhancements under a novel rapid high-temperature thermal annealing (HTA) process. One should note that the small particles, for example from 10 nm to 1000 nm, discussed in Fig. 3 did not undergo HTA, but do demonstrate some enhancement after “standard” annealing at temperatures such as in the range of 800 to 850 °C. The particles in Figs. 4A-4E are annealed in temperature ranges in the 1500-1800 °C range. In other embodiments the annealing temperatures may be in the range of 1300 – 2000 °C or higher temperature. Such treatments have been considered in the past as a means to modify the photoluminescence excitation and emission spectrum of the diamond particles, and towards making differently-colored diamond particles (L. Dei Cas, S. Zeldin, N. Nunn, M. Torelli, A. I. Shames, A. M. Zaitsev, .O. Shenderova, Adv. Funct. Mater. 2019, 1808362). It was strongly suspected, however, that the thermal annealing allows for vacancy and nitrogen mobility, and could also serve to relieve lattice damage and distortion arising from the electron irradiation process preceding it. Annealing above 1500 °C also allows for nitrogen mobility and possibly for lattice relaxation of NV centers. Hyperpolarization experiments answer this question strongly in the

affirmative, demonstrating the effect of HTA in enhancing nuclear relaxation times and consequently the saturation DNP efficiencies.

[0038] The experiments in Figs. 4A-4E consider two different HTA sample runs. One can compare the DNP enhancements with the same particles annealed after irradiation with electrons followed by annealing under standard conditions (850 °C, 2 hours) and under different RTA regimes, and find a striking change in relaxation behavior, consequently followed by an increase in polarization transfer efficiency. In order to demonstrate this more clearly, a study mapping the full field dependent relaxation profile of the ^{13}C nuclei in two samples under standard and HTA conditions was performed. The study found that the effective paramagnetic concentration is relieved under HTA treatment, with the electron spectrum becoming narrower and increasing relaxation times at any given polarization field. Figure 4E shows fluorescence spectra for 18 um particles irradiated and annealed under standard conditions and under HTA, indicating that the HTA conditions cause the particles to be less optically bright in red/NIR spectral range, and demonstrate that the conditions for optimal fluorescence and MRI brightness are generally different. The decay curves in Figure 4C demonstrate that the enhancement gains due to the HTA process stems from an increase in the ^{13}C relaxation times.

[0039] The two representative classes of samples consist of those irradiated at $D_1 = 1.5 \times 10^{19} \text{ e/cm}^2$, shown in Figs. 4A and 4B, and D_2 at the maximum fluence level $D_2 = 5 \times 10^{19} \text{ e/cm}^2$, shown in Figs. 4C-D, possessing close to the largest NV^- center concentration.

Observations, such as shown in Figs. 4A and 4D showing mass normalized ^{13}C spectra, indicate that HTA in the 1700-1800°C range can consistently lead to large improvements in the hyperpolarization levels over conventional annealing at 850°C. For the D_1 samples HTA boosts polarization levels by 2.5 fold, while for the D_2 samples, originally close to worst

performing in Figure 2D, one finds a large 36-fold increase as shown by the arrow 50 in Fig. 4E in the magnitude of DNP enhancement levels under optimal 1720°C HTA. This allows these samples to leapfrog to the best overall for hyperpolarization despite initially showing very poor performance. If employed in ^{13}C hyperpolarized MR imaging, this would correspond to a substantial acceleration just by changes in the annealing conditions.

[0040] These large gains are at once surprising and technologically significant, since annealing at 1720°C is not substantially more technically challenging than at 850°C, and time and temperature control opens new parameter spaces for lattice defect manipulation.

[0041] One should note that a wide range of temperature conditions, anywhere in the 1200-1800°C range, could yield substantial DNP improvements. Interestingly, short-time post-annealing a sample originally annealed at 850°C at 1400°C for 1 hour can already increase DNP levels by 11-fold as shown by line 52 in Fig. 4D. The data also reveals the importance of relatively rapid HTA, extended annealing for instance 50 minutes can lead to significantly degraded performance shown at line 54 in Fig. 4D. It was observed that the exact environment of the annealing does not matter strongly, although an H_2 atmosphere is marginally better and can serve to reduce diamond graphitization. The 36-fold increase in Fig. 3E only quantifies the increase due to the rapid HTA considering identical starting samples at dose D_2 . It is interesting nonetheless that this optimal HTA sample, performs better than any of the samples considered in this study, 1.33 times better than the low dose D_1 . It is anticipated that HTA will also benefit these latter samples. The best DNP performance corresponds to a bulk ^{13}C polarization 0.28%, shown in Fig. 4A, is the highest reported optical hyperpolarization level on crushed particles < 20 μm in size. Finally, the data in Fig. 4A-D strongly indicate that these DNP signal boosts can be explained at least partially by the strong (2-9 fold) increase in ^{13}C relaxation times as a result of HTA. This is

most evident in the representative polarization decay curves in the inset of Fig. 4D. One can also observe a measurable increase in the polarization injection rates under HTA in the inset in Fig. 4C.

[0042] HTA applied on a sample with higher irradiation dose (D2) as compared to the samples treated at D1 dose, provides dramatically large hyperpolarization enhancements over standard treatment, which when size weighted is the best ^{13}C enhancement value reported in literature. NV concentration for the sample irradiated to the dose D2 with best enhancement after HTA treatment is about 7 ppm, while NV concentration for the same sample after standard annealing is about 12 ppm. Comparing samples from the same stock, with the same size and NV concentration, but treated under standard and HTA treatments, it was discovered that the hyperpolarization is enhanced over an order of magnitude in the HTA treated sample. Experiments also revealed that the HTA treatment is generally sensitive to both temperature as well as time of the treatment. Optimal temperature conditions were empirically found to be in the range from around 1700 °C to 1750 °C, and vary approximately between 3 minutes and 15 minutes. It is believed that longer annealing has deleterious effects on the hyperpolarizability of particles due to annihilation of NV. However, some embodiments may have annealing times in the range of 1 to 60 minutes at temperatures in the range of approximately 1300-2000 °C or higher. In one embodiment the HTA can be applied to diamond particles containing vacancies created by irradiating with electron beam or using other types of irradiation (protons, neutrons, ions, gamma-rays). In another embodiment the HTA can be applied to diamond particles containing NV centers formed by standard annealing. In yet another embodiment several HTA treatments at different regimes can be applied in any order to a sample. In yet another embodiment HTA treatments and electron

irradiation can be alternated to rich the desirable hyperpolarization in combination with multicolor emission in diamond particles.

[0043] The embodiments have undertaken the first systematic study of materials conditions affecting room-temperature optical ^{13}C hyperpolarization in diamond particles. The process has resulted in a report on the best size-weighted diamond particle DNP results in the literature. The embodiments have found conditions that set a diamond particle to be optimally hyperpolarizable. An important conclusion stemming from the study is the central role played by ^{13}C spin lattice relaxation in determining the final saturation hyperpolarization enhancements. This in turn, is predominantly determined by interactions of the nuclei with paramagnetic impurities in the lattice. Low dose electron irradiation can cause less lattice damage to start with, and the use of rapid thermal annealing treatments can relieve lattice distortions, post irradiation damage and satellite paramagnetic defects.

[0044] This enables one to use relatively high NV concentrations (approximately 7 ppm), significantly enhancing the concentration of sources that seed polarization in the lattice, while not suffering from concomitant deleterious effects associated with higher defect concentrations. The range of NV concentrations may be about 1 ppm to 30 ppm, between about 2ppm and about 10 ppm and between about 4 ppm and about 8 ppm. Electron irradiation fluences for production of vacancies can varied approximately between 1×10^{17} e/cm² to 1×10^{20} e/cm² and electron beam energies varied between about 1 MeV and 10 MeV. Initial nitrogen concentration in the starting diamond particles can varied approximately between 10 ppm and 1000 ppm with preferred concentration approximately 50 – 100 ppm. It has previously been demonstrated that increasing ^{13}C concentration, up to approximately 10%, maintains DNP efficiency and increases the obtained hyperpolarization signals by about an order of magnitude. Hence, coupled with ^{13}C enrichment, this work paves the way for the

guided discovery of high quality nanodiamond particles for external hyperpolarization of liquids and for applications as targeted bright-field MRI imaging agents.

[0045] Surface functional groups on diamond particles surface can be varied and adjusted to provide best DNP enhancement and external hyperpolarization of liquids, coatings on particles surface and molecular species. In one embodiment, the diamond particles purified from sp^2 carbon are functionalized with at least one functional group selected from the group consisting of carboxylic, hydroxyl, amino, hydrogen, epoxy, polyethylene glycol, polyglycerol, hydrocarbon chain, hydrocarbon, aromatic, nucleophile, thiol, sulfur, acid, base, and fluoro-containing. In another embodiment, the diamond particles purified from sp^2 carbon are attached to or conjugated with at least one material selected from the group consisting of biological molecules, a targeting molecule, a chemical trap, a nucleic acid, a protein, an antibody, a ligand, a dye, a fluorescent specie, a radioactive specie, a paramagnetic specie, an image contrast agent, an isotope, a drug molecule, and a polymer. Species of the above can contain ^{13}C , ^{19}F , ^{31}P , ^{29}Si , ^1H , and other atoms containing nuclear spin in natural abundance or at the enriched content. Species of the above in principle can be hyperpolarized based on the hyperpolarization transfer from hyperpolarized diamond particles.

[0046] It will be appreciated that variants of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations, or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the following claims.

WHAT IS CLAIMED IS:

1. A method of hyperpolarizing one of either diamond or silicon carbide material, comprising:
 - irradiating particles of the wide band-gap semiconductor material with electron radiation to produce irradiated particles;
 - annealing the irradiated particles of the wide band-gap semiconductor material for a time period in a range of 1 to 60 minutes at a temperature in the range of 1300 – 2000 degrees Celsius to produce annealed particles;
 - selecting ones of the annealed particles having a nitrogen vacancy center concentration lower than 15 parts per million;
 - illuminating the selected particles with laser light; and
 - subjecting the selected particles to at least one of microwave radiation or magnetic field sweeps to produce hyperpolarized particles.
2. The method as claimed in claim 1, wherein the temperature range further comprises 1720 degrees Celsius.
3. The method as claimed in claim 1, wherein the time period further comprises a range of 1 to 15 minutes.
4. The method as claimed in claim 1, wherein the annealing occurs in a hydrogen atmosphere.
5. The method as claimed in claim 1 wherein the illuminating and subjecting occur simultaneously.
6. The method as claimed in claim 1, wherein the subjecting occurs in a low magnetic field in a range of 0.01 T to 10 T, inclusive.

7. The method as claimed in claim 1, wherein the electron radiation has a fluence in a range of 1×10^{18} e/cm² to 5×10^{19} e/cm², inclusive.
8. The method as claimed in claim 1, wherein the electron radiation has a beam energy between 1 MeV and 3 MeV.
9. The method as claimed in claim 1, wherein the electron radiation has a beam energy of 1MeV to 10 MeV.
10. The method as claimed in claim 1, wherein the microwave radiation is swept in frequency between in a bandwidth 0 and 2GHz.
11. The method as claimed in claim 11, wherein the microwave radiation is one of either chirped at 0.1-100 millisecond, in a ramped fashion, or one tailored to the electronic spectrum.
12. The method as claimed in claim 1, wherein the selecting comprises selecting ones in the range of approximately 3-4 parts per million.
13. The method as claimed in claim 1, wherein the selecting comprises selecting ones having nitrogen vacancies in the range of 7 to 8 parts per million.
14. The method as claimed in claim 1, wherein the selecting comprises selecting ones having nitrogen vacancies of approximately between 4 and 8 parts per million.
15. The method as claimed in claim 1, further comprising functionalizing the material with at least one functional group selected from the group consisting of: carboxylic, hydroxyl, amino, hydrogen, epoxy, polyethylene glycol, polyglycerol, hydrocarbons, hydrocarbon chains, aromatic, nucleophile, thiol, sulfur, acid, base, and fluoro-containing groups.
16. The method as claimed in claim 1, further comprising conjugating the material with at least one additional material selected from the group consisting of: biological molecules, a

nucleic acid, a protein, an antibody, a ligand, a dye, a fluorescent specie, a radioactive specie, a paramagnetic specie, an image contrast agent, an isotope, a drug molecule, and a polymer.

17. The method as claimed in claim 16, wherein the material also contains at least one of ^{13}C , ^{19}F , and ^{31}P , ^{29}Si , and ^1H .

18. The method as claimed in claim 1, wherein the material has particles in a size in a range selected from a group consisting of: from 5 nm to 1000 microns, 10 nm to 100 microns, and 100 nm to 18 microns.

19. The method as claimed in claim 1, wherein the material is synthesized from one of a high-pressure high-temperature method; harvesting natural particles; and by chemical vapor deposition.

20. The method as claimed in claim 1, further comprising transferring hyperpolarization from the hyperpolarized particles to nuclei external to the particles.

21. A method of hyperpolarizing one of either diamond or silicon carbide material,, comprising:

irradiating particles of the material with electron radiation to produce irradiated particles;

annealing the irradiated particles of the material for a time period in a range of 1 to 60 minutes at a temperature in the range of 1300 – 2000 degrees Celsius to produce annealed particles;

selecting ones of the annealed particles having a nitrogen vacancy center concentration lower than 15 parts per million;

illuminating the selected particles with laser light;

subjecting the selected particles to one of either microwave radiation or magnetic field sweeps to produce hyperpolarized particles; and

transferring hyperpolarization from the hyperpolarized particles to nuclei external to the particles.

22. The method as claimed in claim 21, wherein the temperature range further comprises 1720 degrees Celsius.

23. The method as claimed in claim 21, wherein the time period further comprises a range of 1 to 15 minutes.

24. The method as claimed in claim 21, wherein the subjecting occurs in a low magnetic field in a range of 0.01 T to 1 T, inclusive.

25. The method as claimed in claim 21, wherein the electron radiation has a fluence in a range of 1×10^{18} e/cm² to 5×10^{19} e/cm², inclusive.

26. The method as claimed in claim 21, wherein the electron radiation has a beam energy of 1MeV to 10 MeV.

27. The method as claimed in claim 21, wherein the microwave radiation is swept in frequency between in a bandwidth 0 and 2GHz.

28. The method as claimed in claim 21, wherein the microwave radiation is one of either chirped at 0.1-100 millisecond, in a ramped fashion, or one tailored to the electronic spectrum.

29. The method as claimed in claim 21, wherein the selecting comprises selecting ones having nitrogen vacancies centers concentration of approximately between 4 and 8 parts per million.

30. A method of hyperpolarizing one of diamond or silicon carbide material, comprising:
irradiating particles having a size having a range of one of either 10 nm to 1000 nm or 100 nm to 1000 nm of the material with electron radiation to produce irradiated particles;

annealing the irradiated particles of the material for a time period in a range of 1 to 120 minutes at a temperature over 800 degrees Celsius to produce annealed particles;

selecting ones of the annealed particles having a nitrogen vacancy lower than 15 parts per million;

illuminating the selected particles with laser light; and

subjecting the selected particles to one of either microwave radiation or magnetic field sweeps to produce hyperpolarized particles.

31. The method as claimed in claim 30, further comprising transferring hyperpolarization from the hyperpolarized particles to nuclei external to the particles.

32. The method as claimed in claim 30, wherein the temperature range further comprises 1720 degrees Celsius.

33. The method as claimed in claim 30, wherein the time period further comprises a range of 1 to 15 minutes.

34. The method as claimed in claim 30, wherein the subjecting occurs in a low magnetic field in a range of 0.01 T to 1 T, inclusive.

35. The method as claimed in claim 30, wherein the electron radiation has a fluence in a range of 1×10^{18} e/cm² to 5×10^{19} e/cm², inclusive.

34. The method as claimed in claim 30, wherein the electron radiation has a beam energy of 1MeV to 10 MeV.

35. The method as claimed in claim 30, wherein the microwave radiation is swept in frequency from 0 to 2 GHz.

36. The method as claimed in claim 30, wherein the microwave radiation is one of either chirped at 0.1-100 millisecond, in a ramped fashion, or one tailored to the electronic spectrum.

37. The method as claimed in claim 30, wherein the selecting comprises selecting ones in below 7 parts per million.

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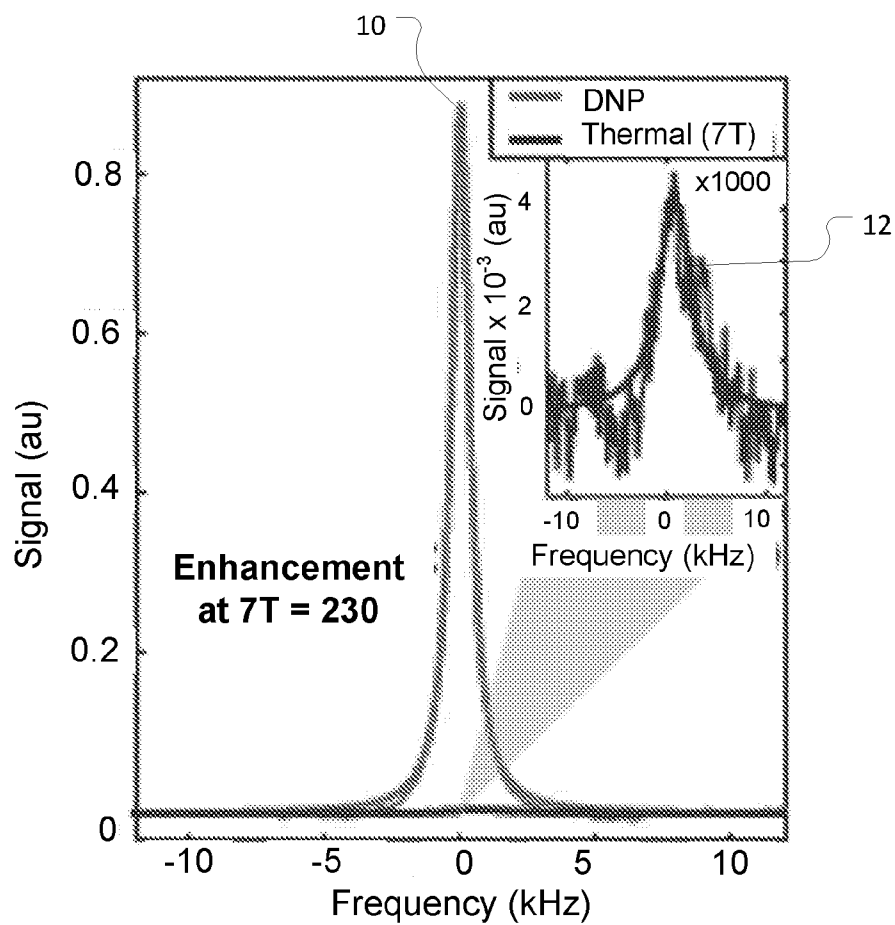


FIGURE 1A

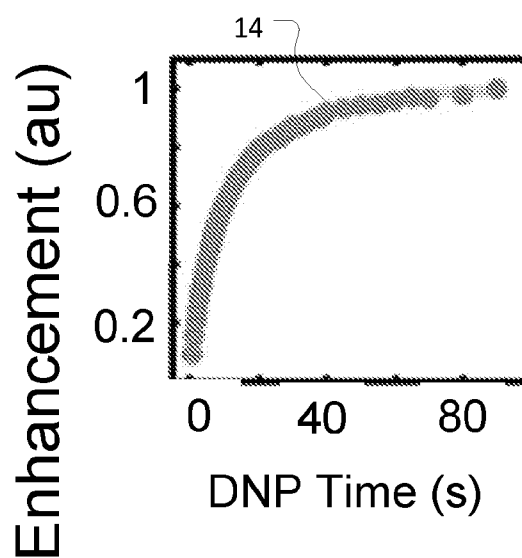


FIGURE 1B

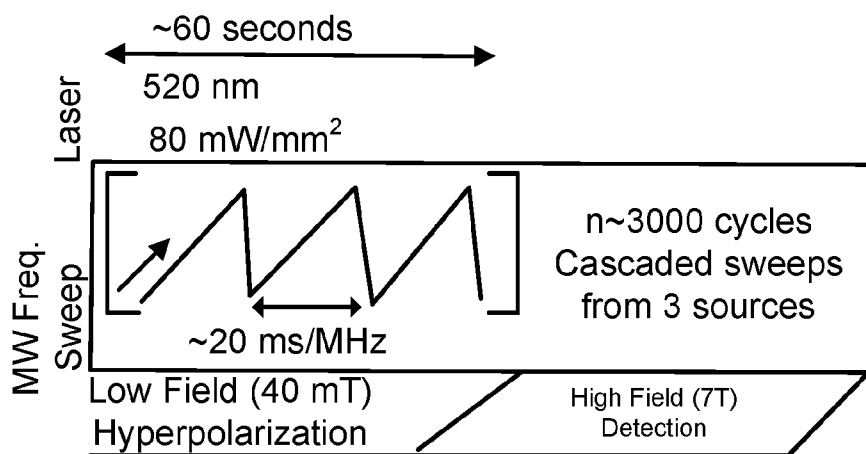


FIGURE 1C

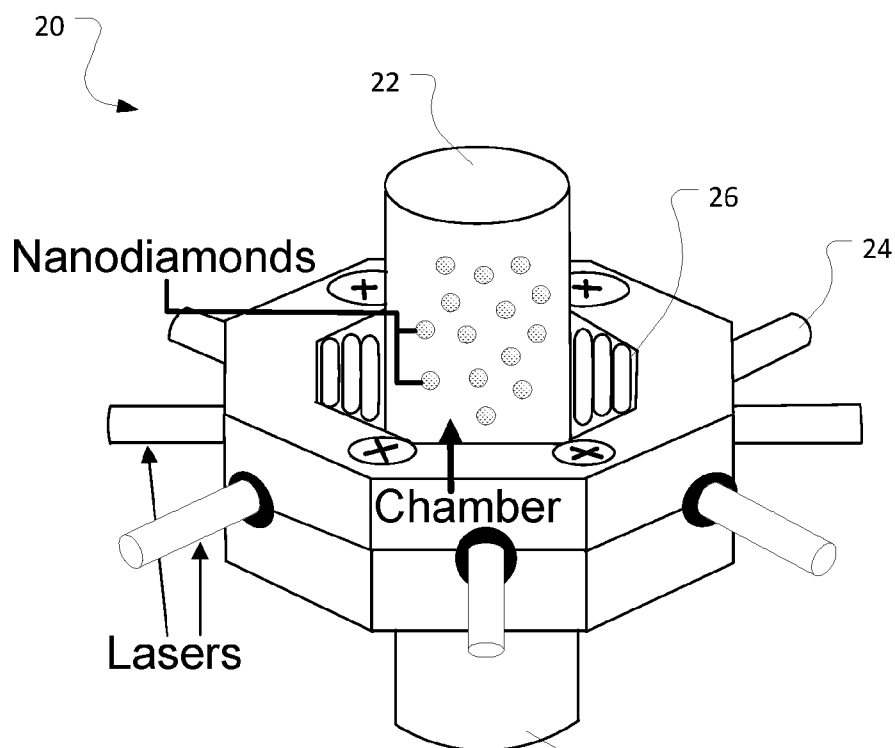


FIGURE 1D

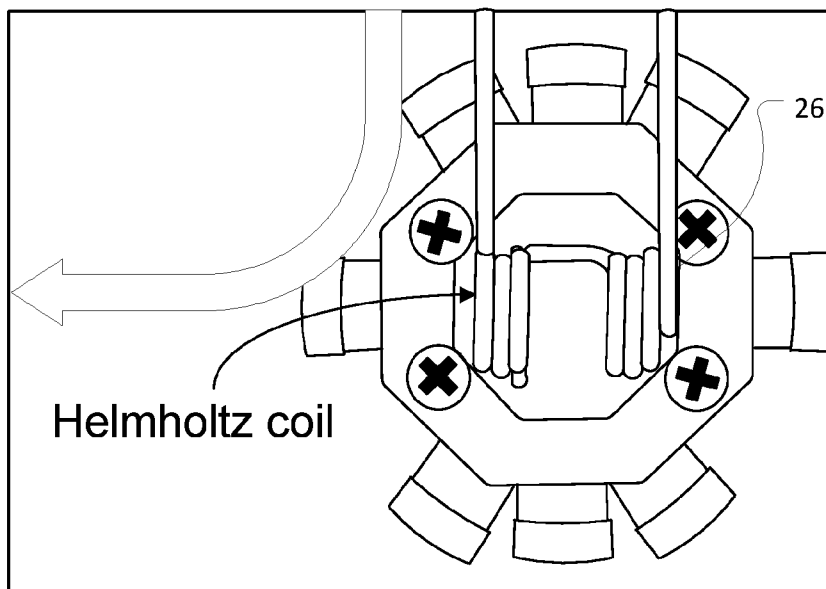


FIGURE 1E

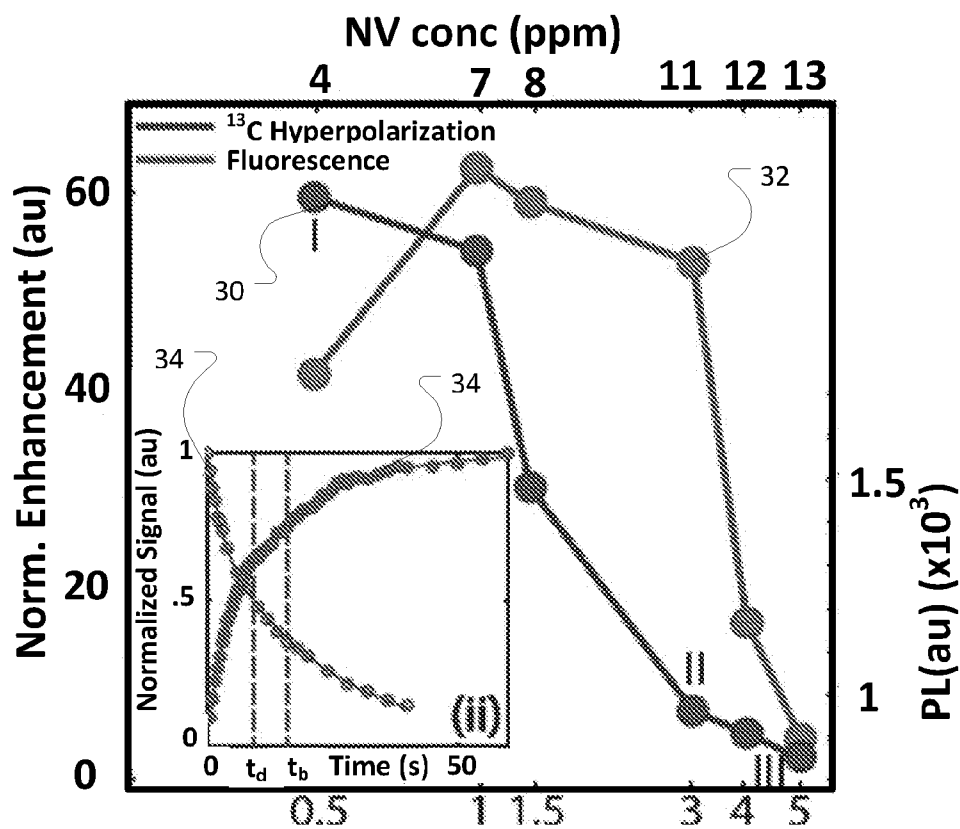


FIGURE 2A

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FIGURE 2B

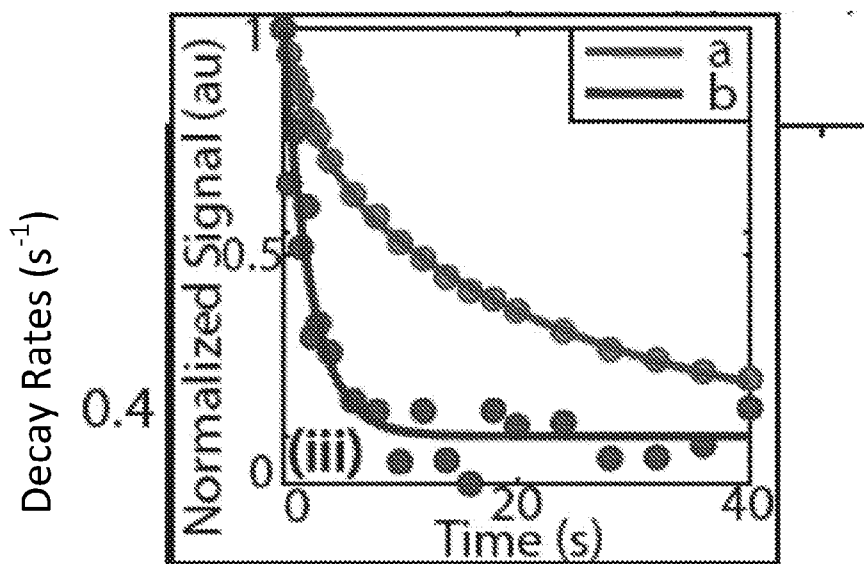
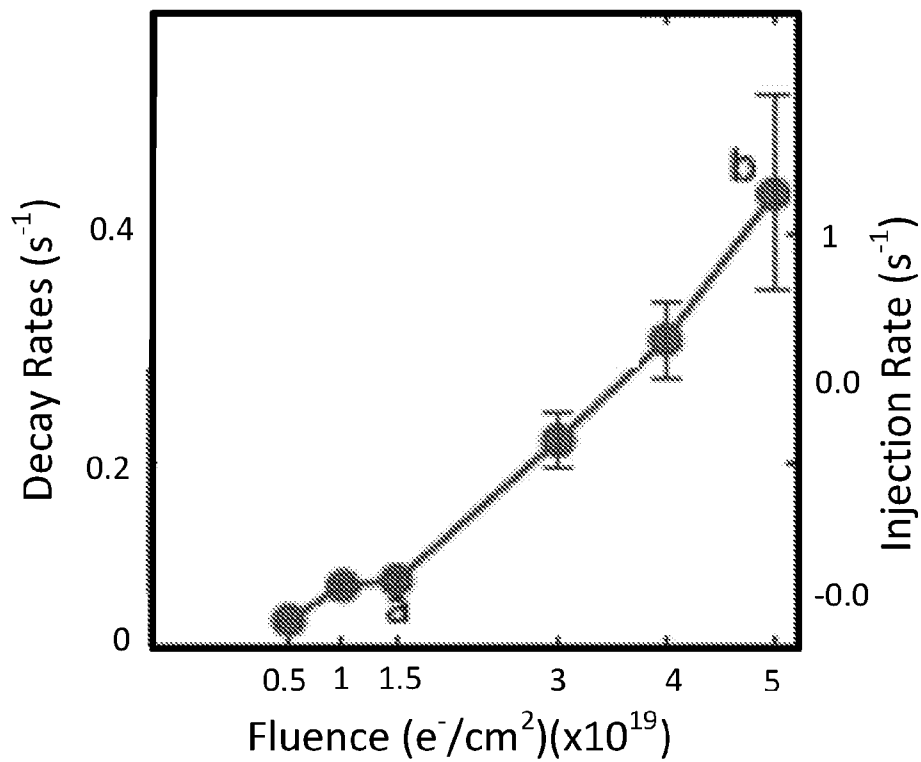


FIGURE 2C

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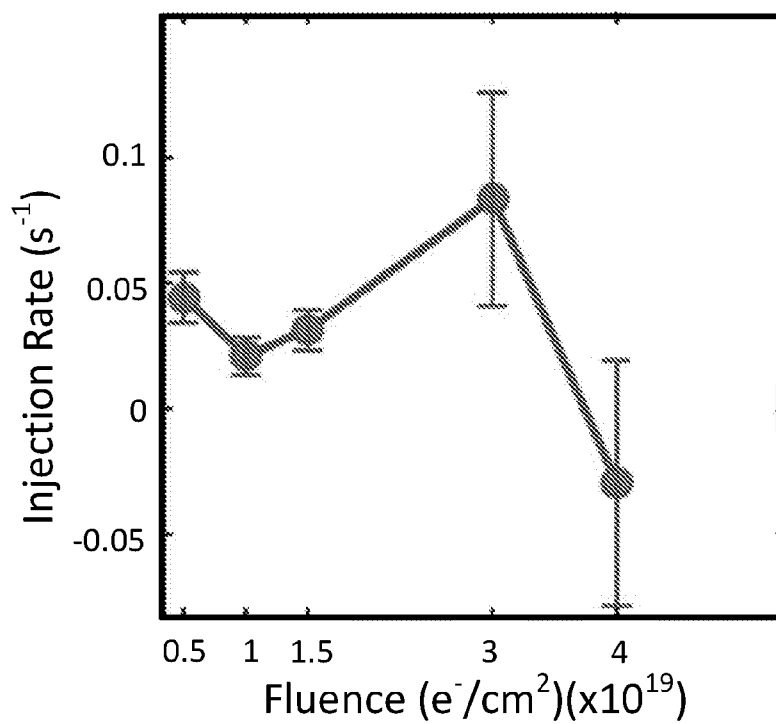


FIGURE 2D

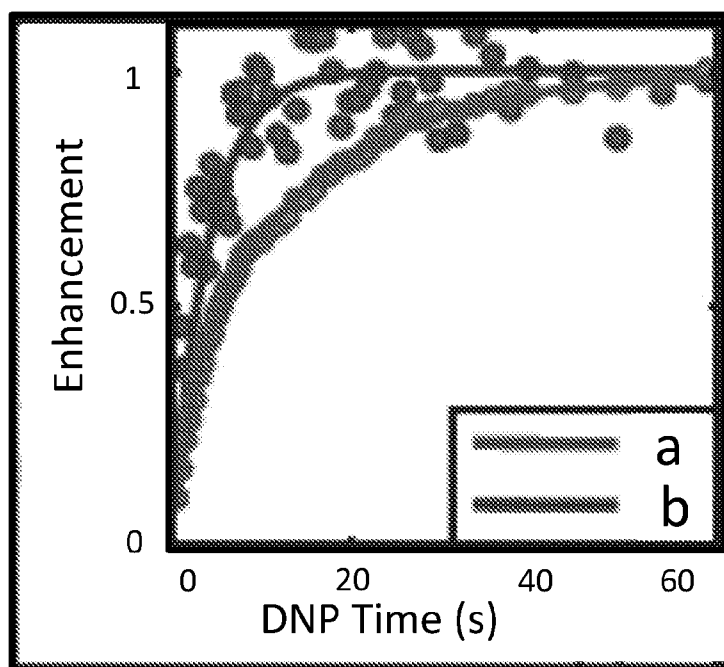


FIGURE 2E

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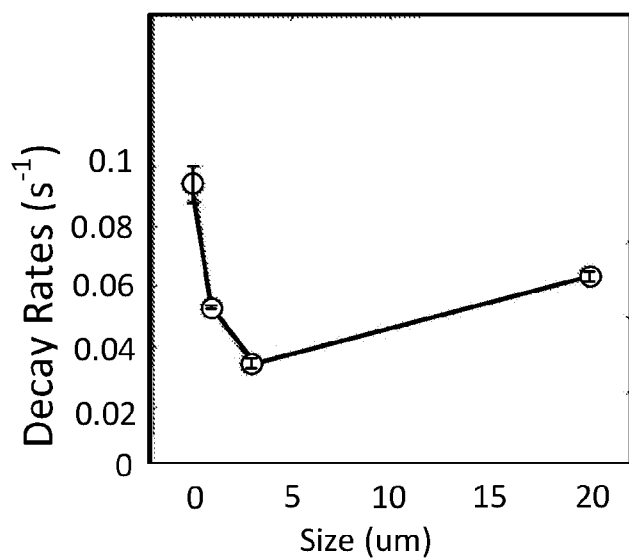


FIGURE 3A

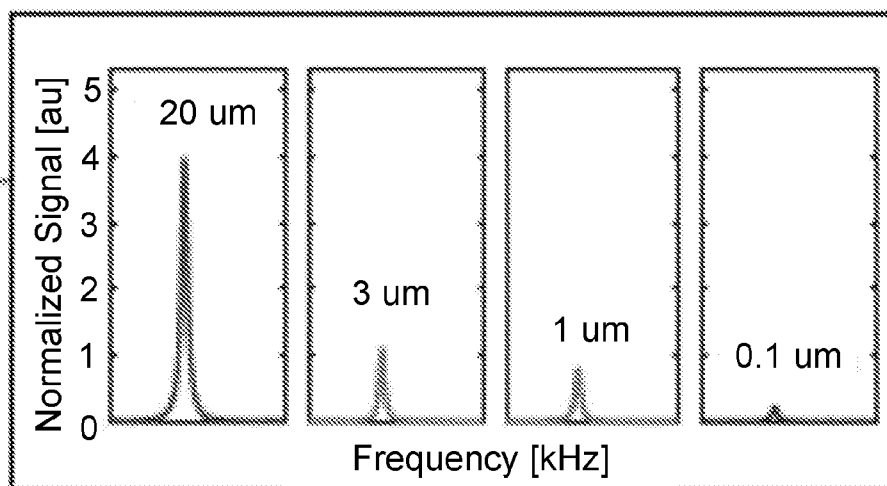


FIGURE 3B

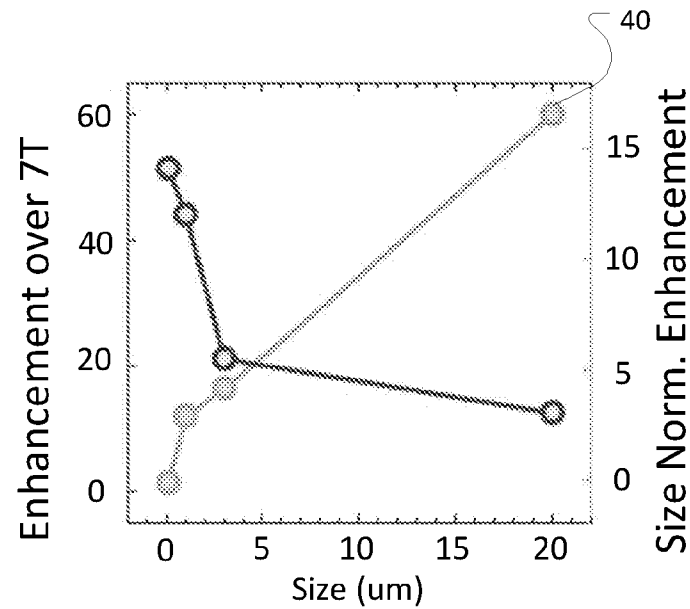


FIGURE 3C

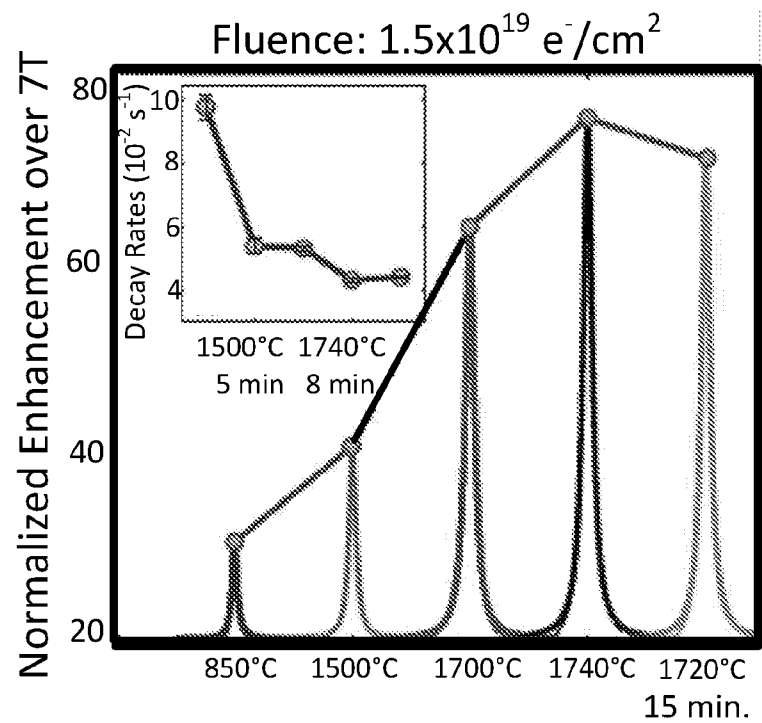


FIGURE 4A

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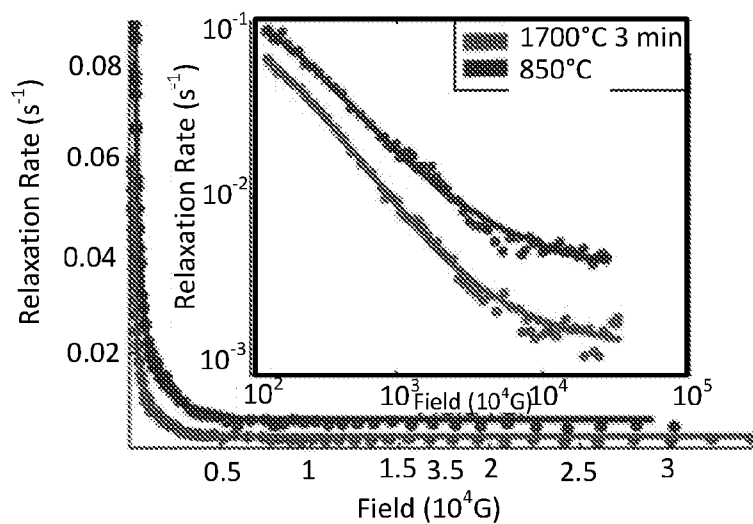


FIGURE 4B

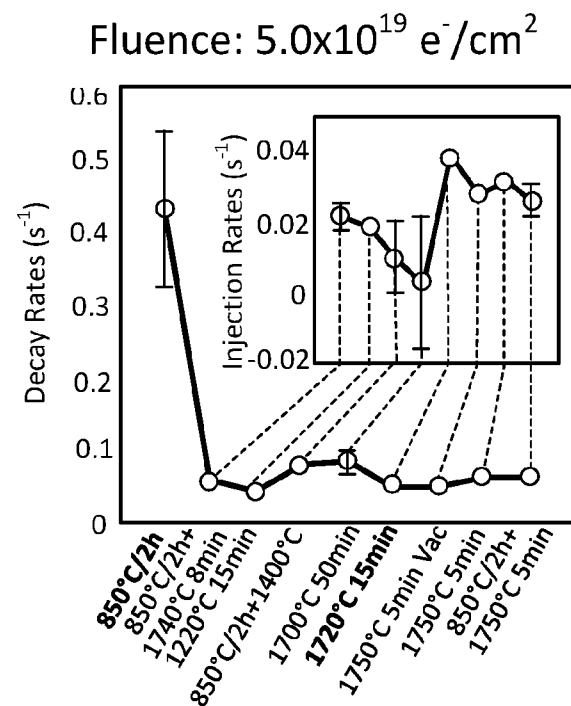


FIGURE 4C

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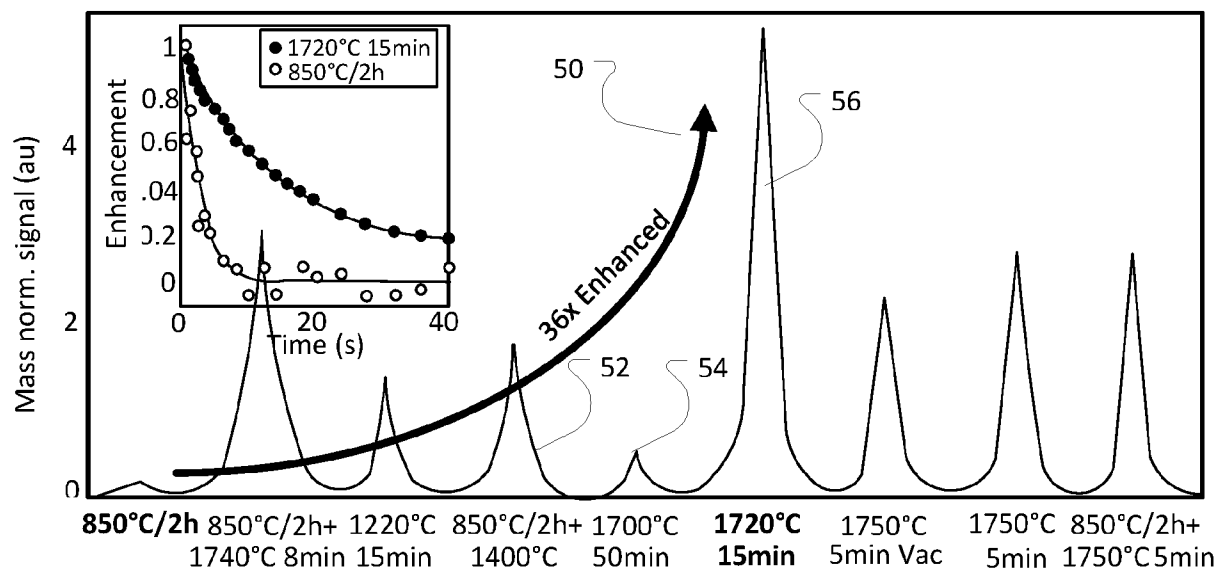


FIGURE 4D

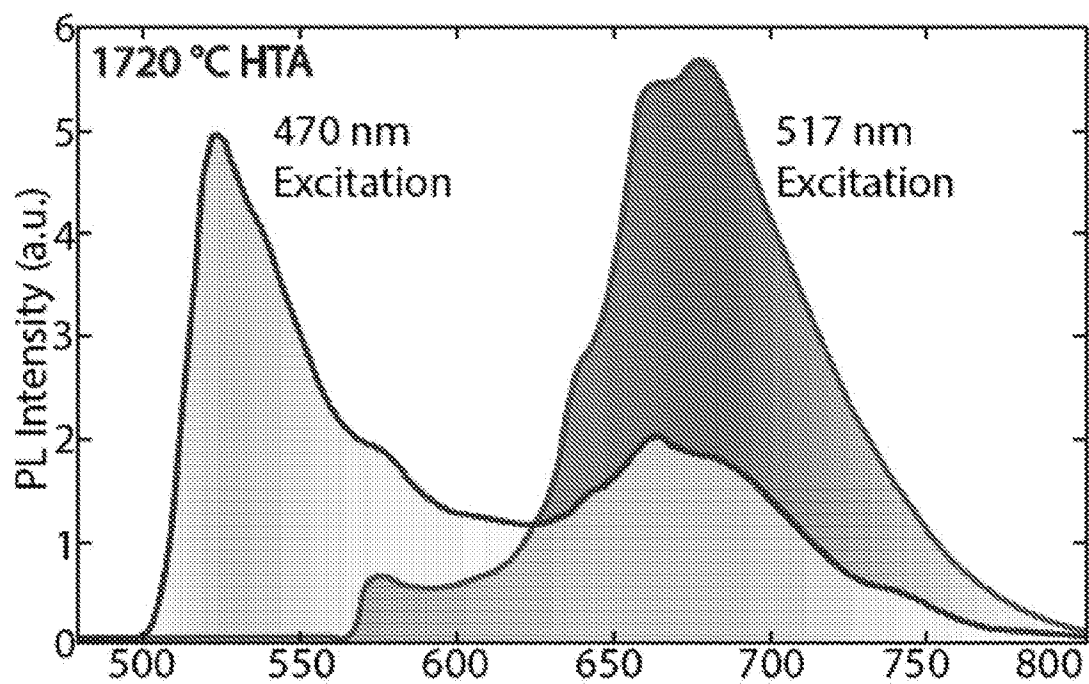


FIGURE 4E

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/32700

A. CLASSIFICATION OF SUBJECT MATTER

IPC - H01L 21/00; H01L 21/28 (2020.01)

CPC - H01L 27/11568; H01L 29/40117; H01L 29/78645; H01L 29/7869

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,880,613 A (Sato et al.) 14 November 1989 (14.11.1989) Abstract; claim 6; col 8 table 1	1-37
A	WO 2010/149775 A1 (Element Six Limited) 29 December 2010 (29.12.2010) Abstract, pg 6 ln 5-20; pg 45 table 8	1-37
A	WO 2019/089948 A1 (The Regents of the University of California) 09 May 2019 (09.05.2019) Abstract; pg 13 claim 1; pg 13 claim 2	1-37
A	US 2018/0028418 A1 (International Technology Center) 01 February 2018 (01.02.2018) Abstract; claim 26; claim 27;	1-37
A	US 2018/0080145 A1 (Element Six Limited) 22 March 2018 (22.03.2018) Abstract; para [0041],	1-37
A, P	WO 2020/015769 A1 (Ustav Organické Chemie a Biochemie AV ČR) 23 January 2020 (23.01.2020) Abstract;	1-37
A, P	WO 2020/081965 A1 (Adamas Nanotechnologies Inc) 23 April 2020 (23.04.2020) Abstract; para [0008]-[0035]	1-37

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Further documents are listed in the continuation of Box C.

☐

See patent family annex.

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"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 July 2020

Date of mailing of the international search report

12 AUG 2020

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Lee Young

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