

A Review Article on Nanodiamonds Discussing Their Properties and Applications

Sheemah Kazi¹

¹(Student of Pharmacy Department of L.I Institute of Pharmacy, Ahmedabad 380007, India)

ABSTRACT: *With the rapid development of Nano science and nanotechnology, a wide variety of nanomaterial have been synthesized and discovered. Diamond nanoparticles, or Nanodiamonds, have the most disparate origins. Diamond nanoparticles are another form of carbon nanomaterial's with unique properties and applications They are found in crude oil at concentrations up to thousands of parts per million, in meteorites, interstellar dust, and protoplanetary nebulae, as well as in certain sediment layers on Earth. They can also be produced in the laboratory by chemical vapor deposition or by detonating high explosive materials [27]. Nano diamonds have excellent mechanical and optical properties, high surface areas and tunable surface structures. Diamond nanoparticles are another form of carbon nanomaterial with unique properties and applications. Here we review the synthesis, structure, properties, and applications of individual Nano diamonds and clusters of Nano diamonds and their biomedical applications.*

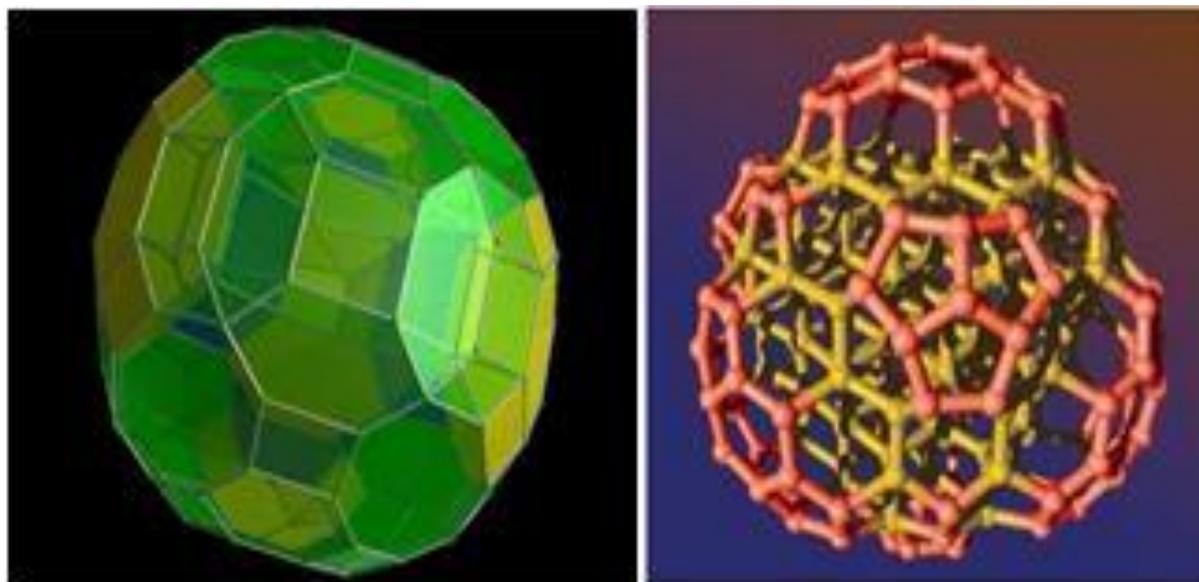
KEY WORDS : *nanotechnology, nanoparticles, Nanodiamonds, detonation*

I. INTRODUCTION

In the last decade not only the sp² carbons like fullerenes, carbon nanotubes came onto focus but the nanoscopic version of the sp³ carbon namely **NanoDiamonds (ND)** has been in the center of attraction for scientists. Historically speaking, Nano diamond is not really a “new” carbon modification. It was already produced back in the 60s by Russian and American scientists. Then, beginning in the late 1990s, a number of important breakthroughs led to wider interest in these particles. There are several methods available for the synthesis of Nano diamonds such as detonation technique, chemical vapor deposition (CVD) etc. An important advantage of NDs is the ease and diversity to which they can be functionalized. Functionalization of NDs with biological molecules, such as peptides, proteins and nucleic acid, has led to practical significance for biomedical applications, covering their use for single particle imaging in cells, drug delivery and protein separation. Nano diamonds (NDs) in particular offer a unique combination of biologically relevant properties that provide possible advantages over other nanoparticles. As a result, NDs are being explored for use in an array of clinical applications from cancer therapy to gene delivery. NDs can be induced to fluoresce by the addition of nitrogen defects through ion irradiation. The particle displays low photo bleaching with high biocompatibility, resulting in a promising candidate for cellular tracking studies. NDs are also viable for in vivo tracking as a powerful magnetic resonance imaging (MRI) contrast agent when coupled with gadolinium [Gd] (III). The features of the ND platform make it highly suitable as a drug delivery agent. In cancer therapy, NDs have exhibited the ability to support steady release of chemotherapeutic drugs. ND drug platforms have also been embedded into thin-film devices, resulting in an implantable patch that is capable of sustained administration of therapeutic treatment agents. Moreover, NDs are also being developed for use in cutting-edge detection techniques such as magneto-optic and scanning single-photon microscopy.

II. STRUCTURE OF NANO DIAMOND

Carbon is unique in the number and the variety of its allotropes due to its valiancy. ND is an allotrope of carbon. NDs are carbon-based materials approximately 2 to 8 nanometers in diameter. Figure 1 shows the



crystal structure of Nano diamonds. The crystal structure of ND consists of two close packed interpenetrating face centered cubic lattices; one lattice is shifted with respect to the other along the elemental cube space diagonal by one-quarter of its length ^[25]. NDs are clustered carbon atoms with both graphitic (sp^2) and diamonded (sp^3) bonds. The two types of bonds can be interchangeable. This interchangeability allows ND particles to be flexible templates, particularly around the curved surface where electrons are unstable.

Figure 1: Crystal Structure of Nanodiamond^[25]

III. SYNTHESIS OF NANODIAMOND

There are several methods for the synthesis of Nano diamonds (ND). They can be synthesized by the detonation technique, laser ablation, High energy ball milling of high pressure high temperature (HPHT), chemical vapor deposition (CVD), autoclave synthesis from supercritical fluids, ion irradiation of graphite and ultrasound cavitation. Out of all these methods listed the first three are used commercially for the synthesis of NDs. The detonation technique is discussed as below.

3.1 Detonation technique

The Nano diamonds synthesized by the detonation technique are often termed as the ultra-dispersed diamonds (UDD). Figure 2 shows the flow chart representation of the Detonation technique. The Nano diamond can be synthesized by the detonating mixture of TNT i.e. trinitrotoluene ($C_6H_5N_3O_6$) and hexogen ($C_6H_6N_6O_6$) i.e. RDX and from the remaining soot of the explosion.

The detonation takes place in the closed chamber filled with water (ice) as coolant or inert gas. The diamond yield after detonation crucially depends on the synthesis condition and especially on the heat capacity of the cooling medium in the detonation chamber (water, air, CO_2 , etc.). The higher the cooling capacity, the larger the diamonds yield, which can reach 90%

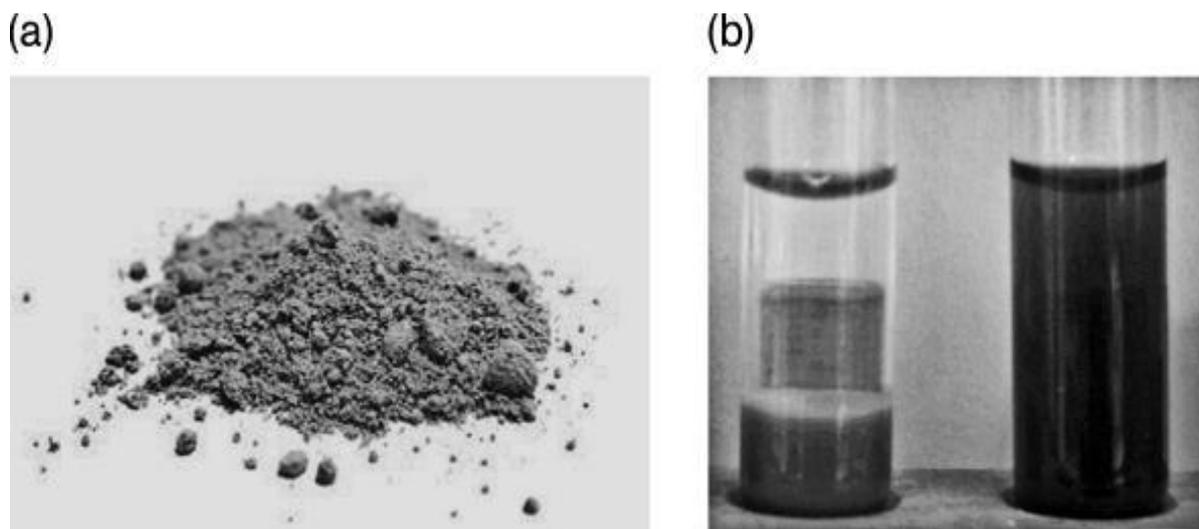


Figure 2: Flow Chart Representation of the Detonation Technique

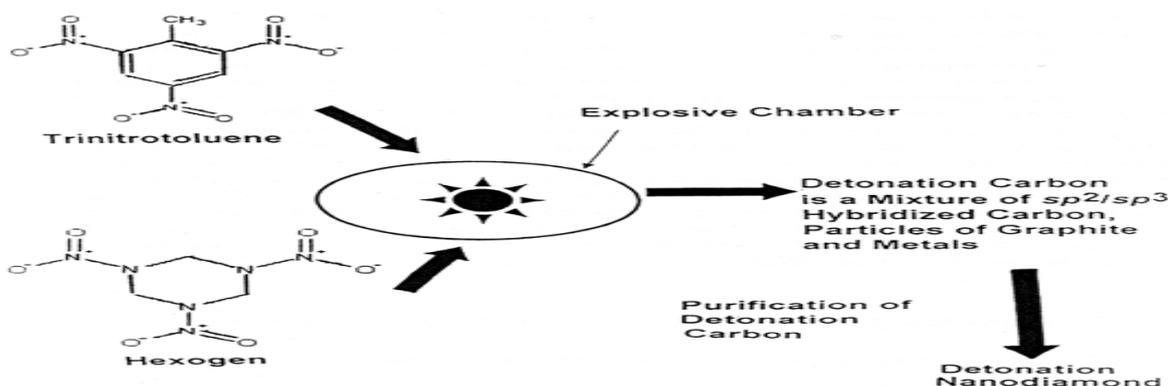


Figure 3(a) : Detonation diamond as powder^[26]

3(b): Ddetonation diamond as unstable suspension in water and as completely DE agglomerated dispersion in water

After the synthesis the diamonds are extracted from the soot by using high pressure high temperature (autoclave) the purification of the detonation soot can be carried out with the help of liquid oxidants (such as HNO_3 , a mixture of H_2SO_4 and HNO_3 , $K_2Cr_2O_7$ in H_2SO_4 etc.) to remove non diamond carbon. To remove non-carbon impurities to <0.5 wt% level, the purified product is subjected to HCl and other treatments. Liquid-phase purification is both hazardous and expensive, contributing up to 40% to the product cost.

Various measurements, including X-ray diffraction and high-resolution transmission electron microscopy) revealed that the size of the diamond grains in the soot is distributed around 5 nm. The grains are unstable with respect to aggregation and spontaneously form micrometer-sized clusters. The adhesion is strong and contacts between a few Nano-grains can hold a micrometer sized cluster attached to a substrate.

IV. PROPERTIES OF NANODIAMONDS

The Nano diamonds have promising properties which make it a useful material in various fields. The following are the exceptional properties of Nanodiamonds. The **hardness** of the diamond is about 50 times more than that of the titanium and stainless steel. The hardness of the diamond makes its useful in the cutting tools and implants. Table 1 shows the comparison of engineering properties between CVD diamond, Titanium and Stainless Steel. For the Nano diamonds, to find their applications in the biology chemical inertness is

important factor. Alloy of Ti6Al4V coated with ND films show that the diamond films have a very good chemical resistance to the corrosive liquid. Biocompatibility cannot be neglected when diamonds are applied to the biology.

Table-1 Comparison of Engineering Properties between CVD diamond, Titanium and Stainless Steel

Properties	CVD diamond	Titanium	Stainless steel
Hardness(kg/mm ²)	10,000	230	210
Young's modulus(GPa)	1000	120.2	215.3
Bulk modulus(GPa)	442	108.6	166
Thermal conductivity(watts/cm *C)	20	0.21	0.16
Thermal expansion($\times 10^{-6}$ K ⁻¹)	1.1	1.8	17.2

The **biocompatibility** of the Nano diamonds was investigated by Yu and coworkers using fluorescent Nano diamond powders with size of 100 nm size and found low cytotoxicity in kidney cells .Then after Schrand and coworkers found out that Nano diamonds with size of 2-10 nm are not toxic to variety of cells through mitochondrial function and luminescent ATP production assays .It was found that morphology of cells remain unaffected with incubation with NDs. Moreover it has excellent optical properties to be used as bio-label or biomarker. Chemical modification of diamond surface is essential for diamond to be applied as potential biosensor or biochip or a substrate to immobilize biological molecules .Diamond surface can be hydrogen-terminated by exposing the surface to 13.5-MHz inductively coupled hydrogen plasma at 800°C (*Thoms et al., 1994*). With the hydrogen-terminated Nano crystalline diamond, Yang and coworkers successfully designed a chemical procedure to attach DNA onto the diamond surface ^[26]. Its tiny size has given the advantage of large surface area. Furthermore, it has an outstanding photo luminescence.

V. APPLICATIONS OF NANODIAMONDS

- Nano diamonds are useful in polishing of gems, ceramics, glass and silicon wafers and surgical knives .it is used in different concentrations in pastes, slurries and gels for the polishing of computer hard discs, lenses, prisms etc. It is also used as filler to improve the elasticity, strength, heat conductivity and optical characteristics of polymers.
- NDs can be employed to improve the thermal conductivity .The NDs can be added as an additive in the coolant which helps to prevent the hot zones inside the coolant. Hence using NDs in pastes glues and substrates provides an exceptional opportunity of avoiding burnout ,increasing speed of active element reducing the sizes and increasing their reliability and durability
- The NDs can be formulated as the dental material can be used for filling, veneer and reconstruction .The NDs can provide additional mechanical strength and appearance as that of the natural enamel on drying. NDs are known to cure gum diseases hence can be formulated in the toothpaste. As the NDs have excellent absorption properties they can be formulated into the skin care products such as facial tissue lotion, dermal strip, deodorants, skin cleansers, soap and exfoliates. NDs can improve the penetration of the active ingredient into the skin enhancing its therapeutic activity and showing improved results. NDs can be formulated into shampoos too. Another application of NDs is that they can be formulated into nail polishes, eye liners, lip-gloss etc. Using NDs in their formulation improves the durability of the applied formulations. Specifically nail paint with NDs have three to ten times more durability then the normal nail lacquer.
- Due to the excellent properties of NDs such us hardness, chemical inertness, and low cytotoxicity they can used as coating material in implants and other surgical tools in biomedical field .So far the implants done with coating of NDs have not shown rejection hence they can be used successfully
- The chemical modification and surface properties of the NDs allow them to be applies to immobilization of protein and DNA for purification, separation and further analysis .A successful separation of Ca²⁺ activated photo protein and apoobelin and recombinant lucifersae from bacterial cells of E.coli through physical

absorption of proteins on ND were carried out. The traditional method takes several days while the procedure using ND took 30-40 minutes. This study was carried out by bonder and fellow workers.

- Activated charcoal is used for its adsorption properties and small particles size on the other hand NDs also have exceptional adsorptive properties they can adsorb water up to four times their own weight. Each carbon atom on the surface of ND has at least one free electron which may bind to elements such H, O, or N. This makes NDs an excellent adsorbent for amino acids, proteins, platelets and DNA.
- The presence of nitrogen–vacancy (NV) centers — a nitrogen atom next to a vacancy — in Nano diamond leads to useful fluorescence properties. Nanodiamonds emit bright fluorescence at 550-800 nm from nitrogen-vacancy-centers produced by high-energy ion beam irradiation and subsequent thermal annealing. The emission, together with no cytotoxicity and easiness of surface functionalization, makes Nano-sized diamonds a promising fluorescent probe for single-particle tracking in heterogeneous environments as well as can be used as biomarkers and in biolabelling.
- The uptake of NDs by living cell facilitate the use of NDs as drug carriers and delivery vehicles. they are nontoxic and the body's immune systems doesn't attack them. They can bind to a variety of molecules and can give targeted drug release. Furthermore, drug ND complex does not affect the white blood cell this is useful in the cancer treatments. A chemotherapeutic agent such as doxorubicin has been successfully functionalized with NDs and has given effective results as well.
- Utilizing the inherent surface chemistry of detonation Nano diamonds, an amine-functionalized Gd (III) complex was covalently bound allowing visualization of Nano diamond particles by MR imaging. The reflexivity of the Gd (III) contrast agent increased nearly 10-fold in comparison to the free agent upon conjugation to the Nano diamond platform.
- Nano diamonds can be used as an effective gene carrier also. They can furthermore be used for the administration of growth hormone such as insulin.

VI. CONCLUSION

The unique ND properties have demonstrated exceptional performance in various fields. It can be produced in bulk quantities, can be functionalized non covalently and covalently and so far did not show any bio hazardous effects. This makes it a prospective material for a variety of biomedical applications, such as labeling or targeted drug delivery. On the other hand, its mechanical and electronic properties are attractive for the production of various composite materials, either with polymer or metallic matrices. The wide range of potential applications for Nano diamonds will continue to drive research in this field forward. Better understanding of their structure and surface chemistry will lead to greater control over their properties, and also help to increase manufacturing volumes, possibly to levels that will surpass those of fullerenes and other carbon nano material. The search for new ways to make Nano diamonds will also continue, and any increase in supply will almost certainly lead to new applications.

REFERENCES

- [1] Danilenko, V. V. On the history of the discovery of Nano diamond synthesis. *Phys. Solid State* **46**, 595–599 (2004).
- [2] Greiner, N. R., Phillips, D. S., Johnson, J. D. & Volk, F. Diamonds in detonation soot. *Nature* **333**, 440–442 (1988).
- [3] Ozawa, M. *et al.* Preparation and behavior of brownish, clear Nano diamond colloids. *Adv. Mater.* **19**, 1201–1206 (2007).
- [4] Chang, Y. R. *et al.* Mass production and dynamic imaging of fluorescent Nano diamonds. *Nature Nanotech.* **3**, 284–288 (2008).
- [5] Mochalin, V. N. & Gogotsi, Y. Wet chemistry route to hydrophobic blue fluorescent Nano diamond. *J. Am. Chem. Soc.* **131**, 4594–4595 (2009).
- [6] Maze, J. R. *et al.* Nano scale magnetic sensing with an individual electronic spin in diamond. *Nature* **455**, 644–647 (2008).
- [7] Krueger, A. Diamond nanoparticles: Jewels for chemistry and physics. *Adv. Mater.* **20**, 2445–2449 (2008).
- [8] Zheng, W. W. *et al.* Organic functionalization of ultra-dispersed Nano diamond: Synthesis and applications. *J. Mater. Chem.* **19**, 8432–8441 (2009).
- [9] Spitsyn, B. V. *et al.* Inroad to modification of detonation Nano diamond. *Diamond Relat. Mater.* **15**, 296–299 (2006).
- [10] Behler, K. D. *et al.* Nano diamond–polymer composite fibers and coatings. *ACS Nano* **3**, 363–369 (2009).
- [11] Zhang, Q. *et al.* Fluorescent PLLA–Nano diamond composites for bone tissue engineering. *Biomaterials* **32**, 87–94 (2011).
- [12] Wang, D. H., Tan, L. S., Huang, H. J., Dai, L. M. & Osawa, E. *In-situ* Nano composite synthesis: Arylcarbonylation and grafting of primary diamond nanoparticles with a poly(ether–ketone) in polyphosphoric acid. *Macromolecules* **42**, 114–124 (2009).
- [13] Cheng, J. L., He, J. P., Li, C. X. & Yang, Y. L. Facile approach to functionalize Nano diamond particles with V-shaped polymer brushes. *Chem. Mater.* **20**, 4224–4230 (2008).
- [14] Mochalin, V. N. *et al.* Covalent incorporation of animated Nano diamond into an epoxy polymer network. *ACS Nano* **5**, 7494–7502 (2011).
- [15] Purtov, K. V., Petunin, A. I., Burov, A. E., Puzyr, A. P. & Bondar, V. S. Nano diamonds as carriers for address delivery of biologically active substances. *Nano scale Res. Lett.* **5**, 631–636 (2010).
- [16] Alhaddad, A. *et al.* Nano diamond as a vector for siRNA delivery to Ewing sarcoma cells. *Small* **7**, 3087–3095 (2011).
- [17] Osswald, S., Yushin, G., Mochalin, V., Kucheyev, S. O. & Gogotsi, Y. Control of *sp*²/*sp*³ carbon ratio and surface chemistry of Nano diamond powders by selective oxidation in air. *J. Am. Chem. Soc.* **128**, 11635–11642 (2006).
- [18] Shenderova, O. *et al.* Surface chemistry and properties of ozone-purified detonation Nano diamonds. *J. Phys. Chem. C* **115**, 9827–9837 (2011).
- [19] Schrand, A. M. *et al.* in *Safety of Nanoparticles. From Manufacturing to Medical Applications. Nanostructure Science and Technology* (ed. Webster, T. J.) 159–187 (Springer, 2009).

- [20] Schrand, A. M., Hens, S. A. C. & Shenderova, O. A. Nano diamond particles: Properties and perspectives for bioapplications. *Crit. Rev. Solid State Mater. Sci.* **34**, 18–74 (2009).
- [21] Schrand, A. M. *et al.* Are diamond nanoparticles cytotoxic? *J. Phys. Chem. B* **111**, 2–7 (2007).
- [22] Yang, G. W., Wang, J. B. & Liu, Q. X. Preparation of Nano-crystalline diamonds using pulsed laser induced reactive quenching. *J. Phys. Condens. Mat.* **10**, 7923–7927 (1998).
- [23] Boudou, J. P. *et al.* High yield fabrication of fluorescent Nano diamonds. *Nanotechnology* **20**, 235602 (2009).
- [24] Frenklach, M. *et al.* Induced nucleation of diamond powder. *Appl. Phys. Lett.* **59**, 546–548 (1991).
- [25] Rohit R. Bhosale *et al.* Nanodiamonds: A new-fangled drug delivery system. *Indo American Journal of Pharm Research*.2013;3(12)
- [26] 26..Journal Applied of Pharmaceutical sciences, Khalid Mohamed El-Say, ISSN: 2231-3354
- [27] 27. Giulia Galli *Computer-Based Modeling of Novel Carbon Systems and Their Properties*, Carbon Materials: Chemistry and Physics 3,DOI 10.1007/978-1-4020-9718-8 2,_c Springer Science+Business Media B.V. 2010