

A Study on Physical and Chemical Properties of Detonation Nanodiamond

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Abstract. Using analysis test methods, such as x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and Fourier infrared spectrum (FTIR), x-ray small angle scattering (SAXS), optical correlation spectroscopy (PCS), scanning electron microscopy (SEM) and so on, the researchers systematically studied the detonation nanodiamond (DND)'s physical and chemical properties like crystal structures, surface chemical compositions, surface electrical property and particle size distribution, particle morphology and agglomeration state, etc. The results showed that the crystal structures did not be changed before or after DND disaggregation and dispersion, but the surface chemical compositions, surface electrical property, particle size distribution, particle morphology and agglomeration state all were changed obviously. The systematic data of physical and chemical properties of DND were obtained through the study in this paper, which could provide theoretical basis and technical reference for the application research of DND based on relevant technologies.

1. Introduction

With TNT, RDX and other explosives as carbon source precursors in a high-strength steel closed container, DND is synthesized by nanodiamond through detonation reaction. Studies have shown that DND has stable chemical properties, acid-alkali resistance, corrosion resistance, hydrophilic surface, dual characteristics of super hard materials and nanomaterials, and has been applied in ultra-precision polishing, lubricant additives, composite electroplating, biomedicine, polymer material modification and other fields, and has broad market application prospects[1~7]. Characterizing the physical and chemical properties of DND, is the basis of research on the application all above. And systematically studying DND's physical and chemical properties like crystal structures, surface chemical compositions, surface electrical property and particle size distribution, particle morphology and agglomeration state, etc., which could provide theoretical basis and technical reference for the application research of DND based on relevant technologies.

2. Experiment

2.1. Sample Preparation

The raw material sample of this experiment is the DND produced by a domestic company. It is actually a nanodiamond hard aggregation, in the form of gray powder, known as DND grey powder. The preparation process of nanodiamond dispersion material sample is as follows: put the DND grey powder, grinding aid and deionized water in a ball mill for ball mill, through the ball mill-amentia's



synergy effect, the nanodiamond hard aggregation will be spread out. Then by acid treatment in removing impurity and cleaning, get the water-based DND pulp, after size grading treatment, the pulp turns into water-based DND dispersive material, in the form of dark grey liquid.

2.2. Testing and Characterization

The crystal structure of DND was studied by x-ray diffractometer (D/MAX-EAX, Rigaku, Japan). The surface chemical compositions of DND were measured by x-ray photoelectron spectroscopy (XPS) and infrared spectroscopy. The x-ray small-angle scattering method was used to measure the particle size distribution of DND original particles, and the nano-laser particle size meter (Zetasizer3000HS, Malvern Instrument co., LTD.) was used to measure the particle size distribution of DND in water phase. Anhydrous ethanol was used as dispersing medium, ultrasonic wave was used for dispersing for 15min, samples were taken, and SEM (JSM-5600LV, Japanese Electronics Company) was used to observe the morphology and agglomeration state of DND particles.

3. Results and Discussion

3.1. Crystal Structure

The test results of the crystal structure of DND (before and after dispersion) are shown in Figure 1. On the one hand, it shows that the nanodiamonds are cubic lattice structures before or after dispersion. On the diffraction pattern, {111}, {220} and {311}, these three characteristic diffraction peak positions are the same as ordinary diamonds which are synthesized by static pressure method. But since the average grain size of DND particles is about 4.5nm and their grain size does not change after dispersion, it is far less than the average grain size of ordinary diamonds which are synthesized by static pressure method. All above make the diffraction peaks of DND are wider than those of ordinary diamond. On the other hand, compared with before dispersion, the diffraction peak positions of dispersed nanodiamond does not change, and the crystal structure also does not change, the reason may be that DND is just dispersed from coarse aggregations to small aggregations and single particles in the process of ball mill-amentia's dispersion, and is just modified the surface of small aggregations and single crystals which after depolymerization, thus it does not alter the crystal structure of nanodiamond.

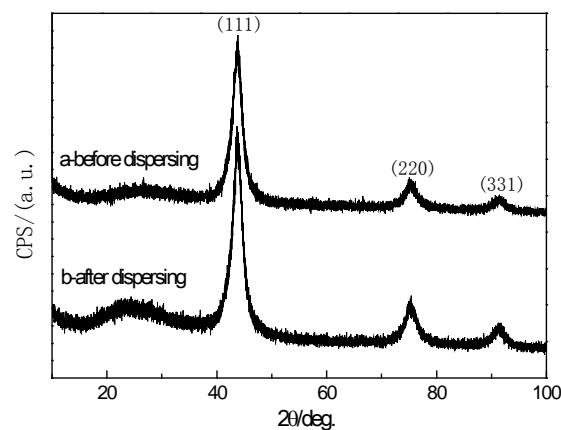


Figure 1. X-ray Diffraction Pattern of DND

3.2. Surface Chemical Compositions

The test results of DND grey powder's surface chemical elements are shown in Table 1. X-ray photoelectron spectroscopy (XPS) analysis showed that the main elements of DND surface are C, O, N, S, among them, the atomic percentage of C is 90.646%, the atomic percentages of O, N, S are 8.090%, 1.135% and 0.129% respectively. Visibly, the sum of atomic percentages of amorphous carbon is 9.354%. The reason is that while the oxygen acid was removing the carbon of non-diamond in the surface of nanodiamond, the oxygen-containing groups were grafted to the surface of

nanodiamond. It is speculated from the XPS oxygen scan, nitrogen scan and nitrogen scan of DND that the oxygen on the surface may exist in the form of carbonyl and hydroxyl, the nitrogen on the surface may exist in the form of amine, nitro and nitride, and the carbon may exist in the form of C-H, C=O and C-C.

Table 1. XPS Analysis of DND Grey Powder

Peak	O1s	N1s	C1s	S2p
Atomic Percentage	8.090%	1.135%	90.646%	0.129%

The influence of different treatments on the infrared spectra of DND is shown in Figure 2. In Figure 2, G represents the nanodiamond grey powder (DG), M represents the nanodiamond sample treated by chemical machinery, and Y and Z represent the sample treated by Y and Z steps.

Sample G has two absorption peaks at 2853.97cm^{-1} and 2922.22cm^{-1} , which can be attributed to C-H vibration, namely, symmetric and asymmetric vibration of $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_3$. In O-H and N-H stretching vibration zones, there is a strong and wide peak of 3433.76cm^{-1} , which may be caused by the stretching vibration of hydroxyl groups on the surface of nanodiamond or hydroxyl groups of carboxyl groups. In addition, there may be amino groups, but their N-H characteristic stretching peak is covered by the peak of hydroxyl groups. The absorption peak at 1629.29cm^{-1} may be formed by the combination of amide peak IvC=O and $\text{II } \delta\text{N-H}+\text{vC-N}$. The absorption peak at 1764.89cm^{-1} (next to 1629.29cm^{-1}) may be the characteristic absorption of the stretching vibration of carboxyl groups' carbonyl groups. In general, the position of this peak is near 1720cm^{-1} , at which time it moves in the direction of high wave number. It may be caused that the α -carbon on the hydroxyl group is directly connected to the electron-absorbing group such as Cl, or there are acid groups on the surface of the diamond. The absorption peak at 1117.43cm^{-1} may be the superposition of the stretching vibration peak of C-OH on the surface of nanodiamond and the stretching vibration peak of C-O single bond of carboxyl group, in addition, the stretching vibration peak of amine C-N is also in this region. The absorption peak at 619.74cm^{-1} may be caused by the stretching vibration of C-Cl peak.

Sample M is the nanodiamond sample treated by ball milling. Compared with G, its carbonyl peak at 1764.89cm^{-1} disappeared, and it is probably caused that the carboxyl group on the surface of diamond generated carboxylate during the ball-milling process, and the carboxylate appeared in the spectrum as two free stretching vibration peaks (1611.74cm^{-1} and 1324.48cm^{-1}). The absorption peak at 1485.50cm^{-1} may be the bending vibration absorption peak of free hydroxyl O-H. It can also be found from Figure 2 that the hydroxyl peak of sample M was significantly weakened and moved in the direction of low wave number. The main reason is that some hydroxyl groups reacted with other ions and the number of hydroxyl groups decreased.

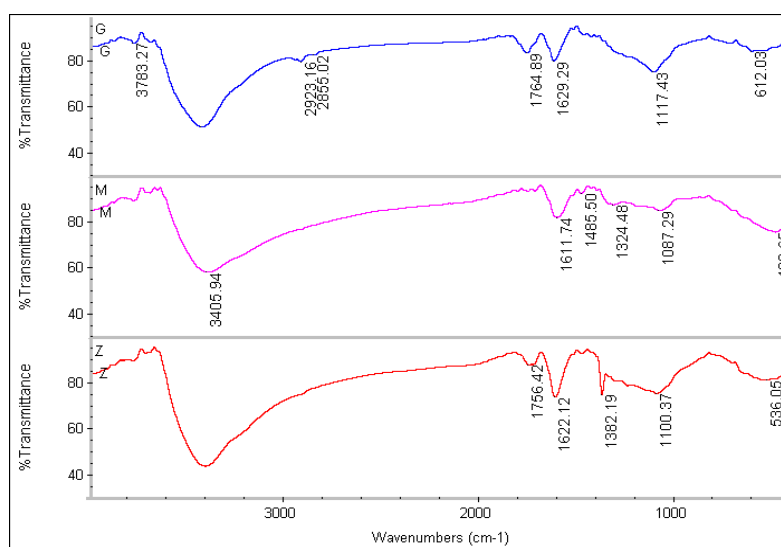


Figure 2. Effects of Different Treatments on DND Infrared Spectra

After acid treatment and impurity removal on sample M, compared with M, since the carboxylic acid anion peak on the surface of nanodiamond disappeared and the carboxyl characteristic peak reappeared, the hydroxyl characteristic absorption peak at 3405.47cm^{-1} was enhanced. In addition, a characteristic absorption peak of 1382.19cm^{-1} appeared, which may be due to the presence of $-\text{NO}_2$ groups on the surface of nanodiamond.

3.3. Surface Electrical Property

Generally, Zeta potential is used to measure the electrostatic repulsion force and dispersion stability of ultra-fine powder in aqueous solution. It is generally believed that when the absolute value of Zeta potential of ultra-fine particles in aqueous solution exceeds 30mV , the dispersion system has good dispersion stability. Because of ionization, ion adsorption and lattice substitution, the surface of DND in aqueous phase is often charged. As shown in Figure 3, Zeta potentials of nanodiamond change with pH values, before or after dispersion, or inorganic electrolyte sodium polyphosphate (STPP) is added after dispersion: When $\text{pH} = 2.5 \sim 11.0$, the Zeta potentials of DND in water medium are in 15 to 33mV , ball mill dispersion can make the Zeta potentials of DND in $22\text{--}36\text{mV}$, and they all increase in the scope of $\text{pH} 2.5 \sim 11.0$; In the range $\text{pH} 2.5 \sim 8.3$, the Zeta potentials of dispersed nanodiamond are more than 30mV , so the system's stability is enhanced; The reason is that the nanodiamond adsorbs more positively charged functional groups on its surface after dispersion, which makes the surface potentials increase; After the addition of STPP, when $\text{pH} = 8.3\text{--}11.0$, the Zeta potentials of nanodiamond below -35mV , and the absolute potential values increase, thus significantly improving the electrostatic repulsion between particles. It can be found that the absolute Zeta potential values of DND can be greater than 30mV by dispersing and adding agentia STPP after dispersion. In the actual application range of $\text{pH} 2.5\text{--}11.0$ of DND, the suspension is in a stable dispersing state.

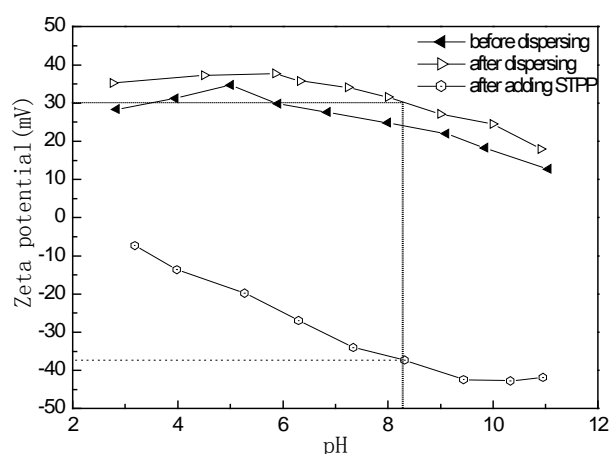


Figure 3. Zeta potentials before and after DND dispersion

3.4. Particle Size Distribution

In Figure 4, we can see the primary particle size distribution curve that SAXS measured DND grey powder: DND average particle size is about 10nm , particle size distribution are all below 60nm . But in Figure 4, we can also see the particle size distribution curve that Zetasizer3000HS measured DND in deionized water: the particle size distribution of DND in water medium is 10 to 8500nm , and most particles above 500nm , less than 20% (wt) of particles under 100nm . That is because in the process of synthesis and drying, nanodiamond is easy to form ultrasonic inseparable hard aggregates through the action of chemical bond force, Van der Waals force, coulomb force, etc. The existence of hard aggregates limits the application of nanodiamond and makes the excellent properties of nanodiamond partially lost. Therefore, it is necessary to disperse and classify nanodiamond in practical application system to meet the needs of practical application.

Figure 5 shows the change of the volumetric particle size distribution curve of nanodiamond in deionized water after ball milling dispersion and particle size classification. Zetasizer3000HS

measured the average particle size of DND grey powder, ball mill dispersion and particle size classification at 364.1nm, 84.7nm and 54.9nm, respectively. From the particle size distribution curve in Figure 5, it can be seen that the particle size distribution of nanodiamond is greatly reduced after dispersion, with about 97% of the particles below 100nm and the maximum particle size at about 230nm. The dispersed nanodiamond suspension was graded to make its particle size distribution below 100nm.

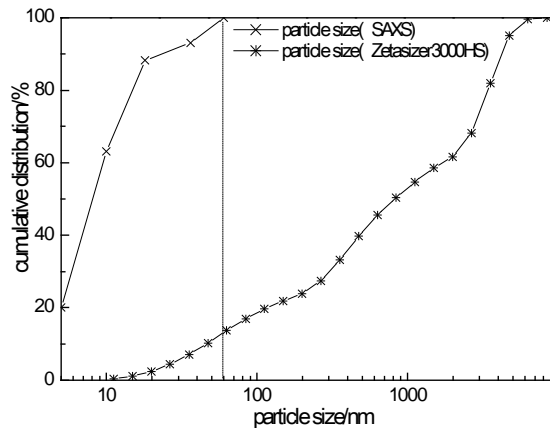


Figure 4. Particle Size Distribution of DND Grey Powder

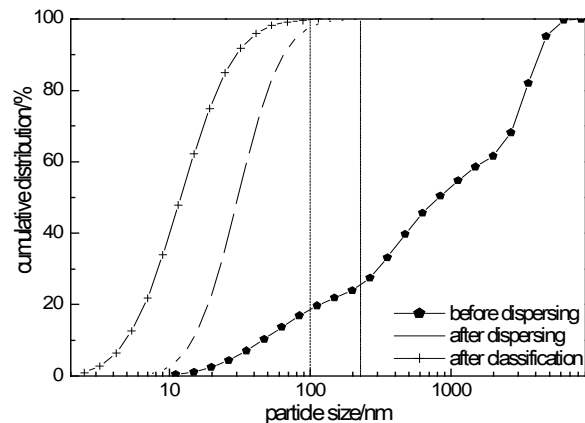


Figure 5. Particle Size Distribution before and after DND Treatment in Aqueous Phase

3.5. Particle Morphology and Agglomeration State

DND ultrasonic wave was fully dispersed in ethanol, and the dispersible solution was dipped in glass rod and glued on the copper plate to make samples, which were naturally cooled and dried, for SEM analysis, as shown in Figure 6. The picture on the left is the SEM photo of DND grey powder, and the observed DND is agglomerate state with the shape of particle snowflake. The picture on the right shows the SEM image of DND grey powder dispersed by ball milling and graded particle size and the observed DND is dispersed and the particles are spherical or quasi-spherical. SEM can directly observe the size, shape and agglomeration performance of nano powder. When the tested sample has good dispersion and no agglomeration phenomenon, SEM can measure the size of the original particle, while conversely, it can measure the size of the agglomeration. Since SEM photographs reflect the size of particles in local areas and cannot reflect the particle size distribution of the whole sample, the author believes that SEM can be used as an auxiliary method to measure the particle size of samples. In addition, SEM is not suitable for particle size detection of some samples that are unstable or even decomposed under intense electron beam bombardment. SEM images showed the particle size of nanodiamond after dispersion and grading, with the shape of spherical or quasi-spherical.

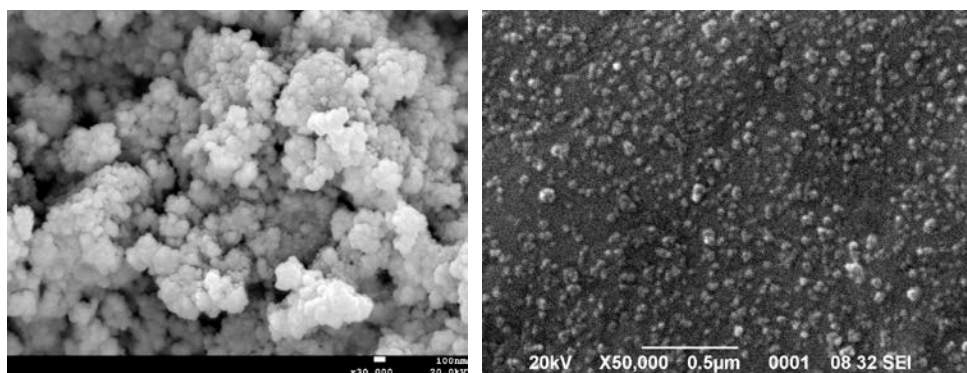


Figure 6. SEM Photos of DND

3.6. Other Physical and Chemical Properties

DND grey powder has been measured by NOVA1000 equipment: specific surface area is $293.6\text{m}^2/\text{g}$, relative density is $3.05\sim 3.30\text{g}/\text{cm}^3$, conductivity is $7.7\times 107\Omega\cdot\text{cm}$, magnetic susceptibility is $1.0\times 10^{-8}\text{m}^3/\text{kg}$, and stomatal area is $1.314\text{cm}^2/\text{g}$.

4. Conclusion

(1)The crystal structure of DND grey powder is cubic lattice structure, and dispersion does not change the crystal structure. The primary particle size distribution was below 60nm. The morphology of the particles is spherical or quasi-spherical, and they are in the state of agglomeration. The specific surface area is $293.6\text{m}^2/\text{g}$, the relative density is $3.05\sim 3.30\text{g}/\text{cm}^3$, the conductivity is $7.7\times 107\Omega\cdot\text{cm}$, the magnetic susceptibility is $1.0\times 10^{-8}\text{m}^3/\text{kg}$, and the stomatal area is $1.314\text{cm}^2/\text{g}$.

(2)The main elements on the surface of DND grey powder are C, O, N and S, among which the atomic percentage of C is 90.646%, the atomic percentage of O, N and S is 8.090%, 1.135% and 0.129% respectively. The functional groups on the surface mainly include polar functional groups such as -OH, -NH₂, -COOH and -NO₂, and a small amount of non-polar functional groups such as -CH₃ and -CH₂CH₃. After ball-milling treatment, the hydroxyl peaks of DND grey powder were obviously weakened and the -CH₃ and -CH₂CH₃ peaks disappeared. Then, after further acid treatment, the characteristic absorption peak of hydroxyl group was enhanced.

(3)In the practical application range of pH2.5~11.0 of DND, the Zeta potential of DND in the water medium is located at 15-33mv, and the absolute value of Zeta potential of DND can be greater than 30mV through dispersion and addition of agent STPP after dispersion, and the suspension is in a stable dispersion state. However, the size distribution of DND in water medium is 10~8500nm, and most of the particles are above 500nm. The average particle size of DND grey powder, ball mill dispersion and particle size classification were 364.1nm, 84.7nm and 54.9nm, respectively. The particle size classification of dispersed nanodiamond suspension could make its particle size distribution below 100nm.

5. Acknowledgement

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