

# Influence of surface modification adopting thermal treatments on dispersion of detonation nanodiamond

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Received 15 October 2004; received in revised form 13 December 2004; accepted 15 December 2004

## Abstract

In order to improve the dispersion of detonation nanodiamonds (ND) in aqueous and non-aqueous media, a series of thermal treatments have been conducted in air ambient to modify ND surface. Small angle X-ray scattering (SAXS) technique and high resolution transmission electron microscopy (HRTEM) were introduced to observe the primary size of ND. Differential thermal analysis (DTA), X-ray diffraction (XRD) methodology, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy were adopted to analyze the structure, bonds at surfaces of the treated ND. Malvern instrument *Zetasizer3000HS* was used for measuring the surface electric potential and the size distribution of ND. As thermal treatments can cause graphitization and oxidization of functional groups at the surface, ND treated at high temperature is correspondingly more negatively charged in an aqueous medium, and the increased absolute value of zeta potential ensures the electrostatic stability of ND particles. Specially, after being treated at a temperature more than 850 K, ND can be well dispersed in various media.

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**Keywords:** Nanodiamond; Agglomeration; Dispersion; Powders; Surface potential; Surface modification; Thermal treatment

## 1. Introduction

Detonation nanodiamond (ND) explosively synthesized from TNT and RDX possesses excellent characteristics such as nano-size with even and round shape, superhardness and chemical stability [1–4]. Therefore, it has great application potentials in many fields of ultrafine polishing, composite plating, lubricant, anti-friction composite materials, low-field electron emission, etc. [5–13]. Physical and chemical properties such as purity, crystal structure, surface composition and dispersion behavior of ND and their corresponding influential factors such as synthesis process, purification

methods and dispersion media have been widely investigated [14–18]. The thermal stability, as well as the surface graphitization of the ND in thermal treatment, has also been studied [19–21].

Although the primary sizes of ND particles stay at around 10 nm [14,18,22,23], they can easily aggregate during synthesis and subsequent treatments, especially when added into a variety of media. Consequently, further deagglomeration and dispersion are necessary. Some techniques such as ultrasonic and surface modification using inorganic electrolytes or hydrophobic organosilyl [24–27], were introduced for deagglomeration and dispersion. The thermal treatment was also used for the dispersion of ND. Xu and Xue [28] adopted a graphitization–oxidation method to actualize the deaggregation and dispersion of ND in aqueous medium. Graphitization was conducted at first in N<sub>2</sub> at 1273 K, whereafter an oxidation treatment in air ambient at 723 K for about 2 h was conducted. After

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that, the powder was dispersed in water with ultrasonic treatment, and a suspension containing over 50% of the particles with a diameter smaller than 50 nm was prepared. But a portion of aggregates, with even coarser size than the original particles was formed during these treatments. They consider that this phenomenon may attribute to the formation of C–O–C bonding (bridged oxygen bonds) between ND crystallites during heat-treatment, and further chemical measures are needed to disperse these particles.

Till now, the effect of thermal treatment on ND properties and the mechanism of the surface modification are not yet very clear. In the work presented in this paper, the surface properties of ND amid thermal treatments and the consequent influence on its dispersion in aqueous and non-aqueous media were investigated. The surface modification of ND has been discussed.

## 2. Experimental and analysis

ND sample used for this investigation was provided by Lingyun Company, a professional detonation diamond producer. This gray powder is one of its purified products from detonation synthesized black powder, where sulfuric acid and perchloric acid were used for purification treatments. Some characteristics of this powder are given in Table 1. In order to investigate the dispersion behavior of sample after thermal treatment, ND samples were loaded in the crucible, put in the stove and heated in air atmosphere with the temperature rising at a rate of  $10 \text{ K min}^{-1}$ , and they were conserved for 30 min after the expected corresponding temperatures were reached, and before they were taken out for further investigation, the samples were cooled along with the stove under the surrounding room temperature. The dispersing media in this study are deionic water and white oil. The deionic water was prepared by adopting the reverse osmosis method and ion exchange technique. The kinematic viscosity of white oil, is around  $5 \text{ mm}^2 \text{ s}^{-1}$  (313 K). Ultrasonic agitation was used for dispersion of particles in the suspensions.

Table 1  
Main characteristics of ND sample

Characteristics (units)	Parameter
Special surface ( $\text{m}^2 \text{ g}^{-1}$ )	293.6287
Density ( $\text{g cm}^{-3}$ )	3.26
Volume resistivity ( $\Omega \text{ cm}$ )	$7.7 \times 10^7$
Surface chemical element (%)	C:89.045, O:8.935 N:1.751, S:0.182 Cl:0.043, Fe:0.035 Si:0.009

Automatic surface area analyzer NOVA 1000 was used to measure the special surface area, with nitrogen as the adsorption medium. Small angle X-ray scattering (SAXS) technique was introduced to test the primary size of the ND dry powder. High resolution transmission electron microscopy (HRTEM) was adopted to observe the size of ND powders and their agglomeration. X-ray photoelectron spectroscopy (XPS) with aluminum radiation was used to analyze the chemical composition at ND surface. Fourier transform infrared (FTIR) spectroscopy was introduced to analyze the functional groups on ND surfaces, using the standard technique of KBr-pellet with Nexus 470 (Thermo Nicolet, USA). X-ray diffraction (XRD) analysis was conducted using diffractometer *D/max-rA* (Rigaku, Japan) with Cu radiation. Differential thermal analysis (DTA) was carried out in air ambient using a thermal analysis system *SDT 2960* (TA Instruments, USA). Malvern's two-in-one system *Zetasizer3000HS* (Malvern Instruments Ltd., UK) was adopted for the measurement of size distribution and ND surface zeta potential. Hydrochloric acid and sodium hydroxide were used as regulators to modify pH value of an aqueous media.

## 3. Results and discussion

### 3.1. Primary size of original sample

Primary particle size of ND was measured adopting SAXS (Table 2). The result shows that this ND sample has a dimension smaller than 60 nm with the mean size of 12.0 nm and the median size of 8.5 nm. 88.3% of the particles are less than 18 nm in diameter. HRTEM micrographs, as given in Fig. 1, show that the primary ND has a nanometer size and serious agglomeration. The size of aggregates is broadly distributed from around 10 nm to more than 1000 nm.

### 3.2. Crystal structure

DTA results, shown in Fig. 2, illustrate the effect of thermal treatment temperature on ND characteristics.

Table 2  
Size distribution of primary ND particles

Size interval (nm)	$f(D)$ (%/nm)	Mass fraction (%)	Cumulative (%)
1–5	5.02	20.1	20.1
5–10	8.60	43.0	63.1
10–18	3.15	25.2	88.3
18–36	0.26	4.7	93.0
36–60	0.29	7.0	100.0

Mean size: 12.0 nm, median size: 8.5 nm.

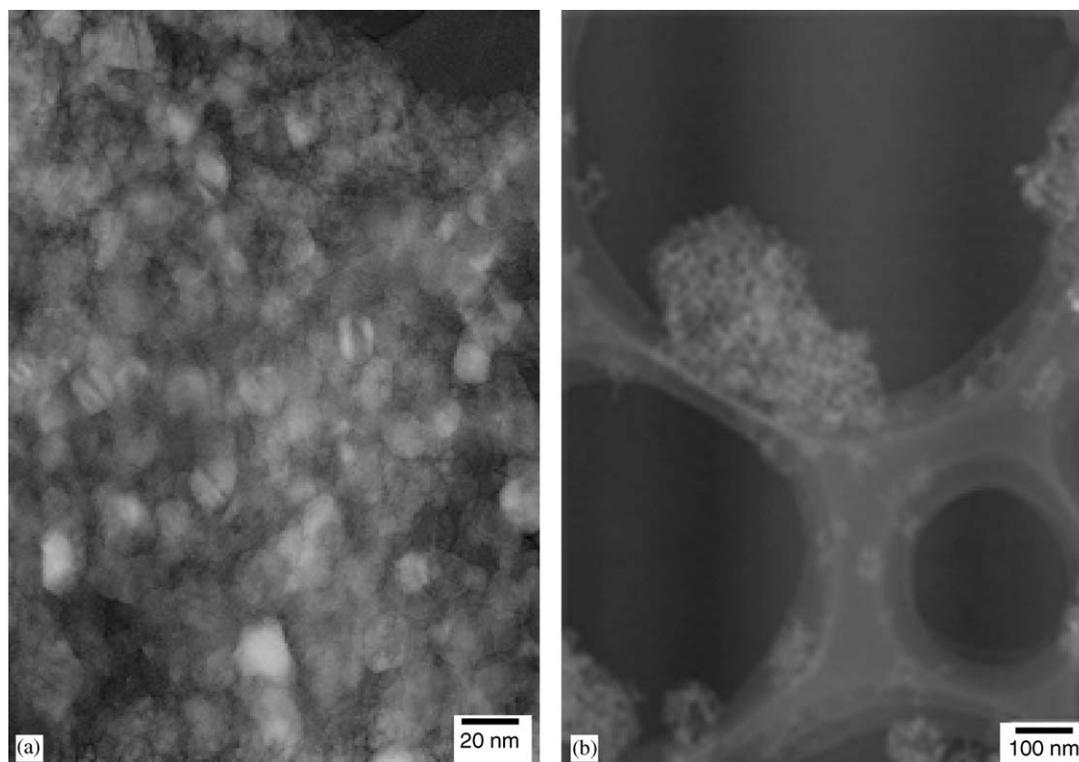


Fig. 1. HRTEM micrographs of ND particles. (a) Primary particle of ND sample is quite uniform in size and shape, and the mean size is around 10 nm; (b) agglomeration and non-uniformity of ND particles.

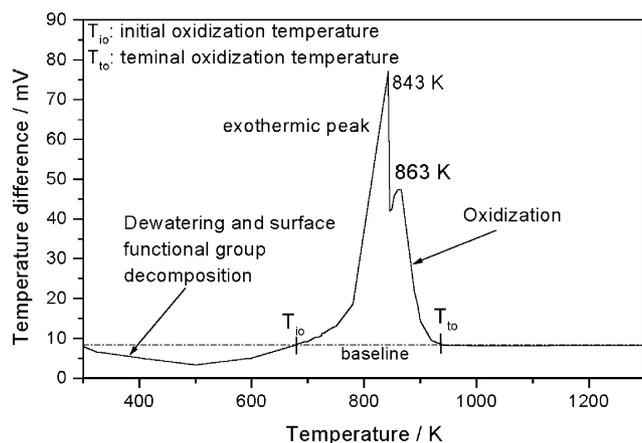


Fig. 2. Differential thermal analysis of ND in air ambient.

The ND sample seems to be endothermic at the beginning of heating process, namely, when the temperature is comparatively low. Dewatering and decomposition of some surface ingredients and functional groups may be the main reasons of this endothermic phenomenon. As the temperature reached around 670 K, obvious exothermic phenomenon occurred (lasted till around 930 K), and two acute exothermic peaks appeared at 843 and 863 K, which may be caused by surface graphitization and oxidation of ND.

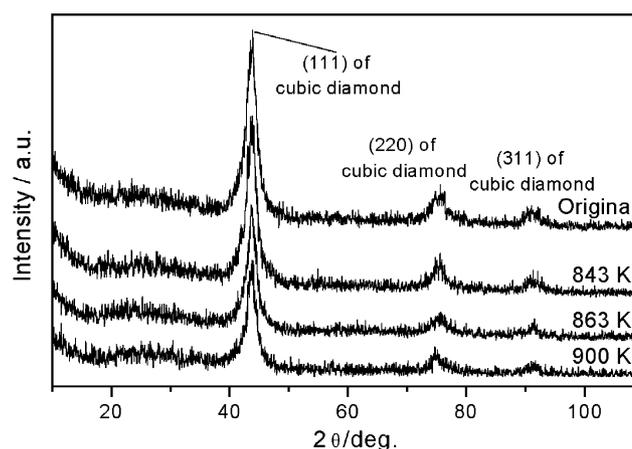


Fig. 3. XRD patterns of ND during thermal treatments, where the intensities of first three peaks of cubic-diamond XRD diffraction become weaker correspondingly along with the increase of heating temperature.

Fig. 3 shows XRD patterns of the original ND and the samples heated in air atmosphere for 30 min at 843, 863 and 900 K. Along with the increase of heating temperature, diffraction intensities of three cubic diamond faces (111), (220), (311) turned to be weaker and the peaks turned to be broader stepwise, which may be caused by the increase of the non-cubic diamond

ingredients in the samples as the heating temperature climbs. The results may indicate the relatively drastic oxidization and obvious surface graphitization during this sensitive temperature range.

### 3.3. Surface functional groups

A transformation of surface functional groups on ND during heating treatments was observed in the FTIR spectra as shown in Fig. 4. The absorption peaks at 2923.16 and 2855.02  $\text{cm}^{-1}$  correspond to the asymmetric and symmetric stretching C–H vibration respectively. And the absorption peak at 3433.76  $\text{cm}^{-1}$  corresponds to the stretching O–H vibration, while that at 1117.43  $\text{cm}^{-1}$  correspond to the deformation O–H vibration. The intensities of these peaks decline stepwise along with the increase of heating temperature.

A distinct trend of the strengthening and a blue shift of C = O stretching vibration of carbonyl groups (from 1764.89 to 1785.80  $\text{cm}^{-1}$ ) can be observed. This may be attributed to the rupture of hydrogen bands and the oxidation of alkane hydrocarbon groups. The distinct vanishing of stretching C–H vibration ( $\nu_{\text{CH}_2}$ ) peak is also caused by the oxidation of alkane hydrocarbon. It can be more intensively oxidized amid thermal treatments in air ambient than in inert gas atmosphere or in vacuum, where the oxidation is restricted [19].

Furthermore, the vibration of ether groups ( $-\text{C}-\text{O}-\text{C}-$ ) is strengthened (around 1269.59  $\text{cm}^{-1}$ ), which may be caused by the formation of ether bonds between adjacent ND particles during the heating, dewatering and powder reagglomeration processes. It is similar to the bonding like C–N–C, which has the same absorption band in FTIR spectra. It may also be formed between ND particles. A possible mechanism of particle interaction is given in Fig. 5.

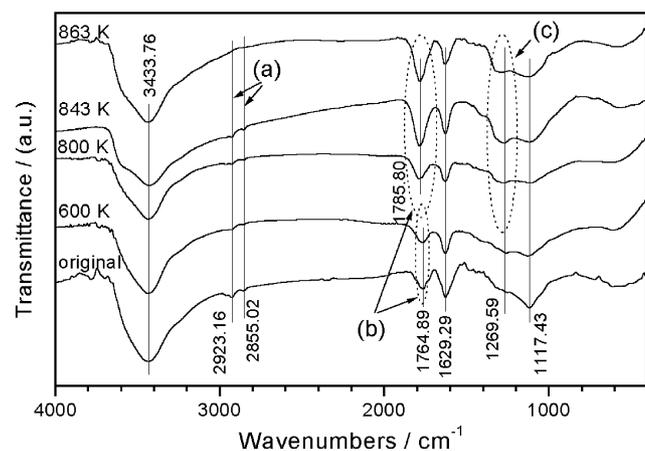


Fig. 4. FTIR spectra of ND sample impacted by the heating temperature. (a) weakening and vanishing of  $\nu_{\text{CH}_2}$  along with the increase of heating temperature; (b) blue-shift and strengthening of  $\nu_{\text{C}=\text{O}}$ ; (c) strengthening of  $\nu_{\text{C}-\text{O}-\text{C}}$  and  $\nu_{\text{C}-\text{N}-\text{C}}$ .

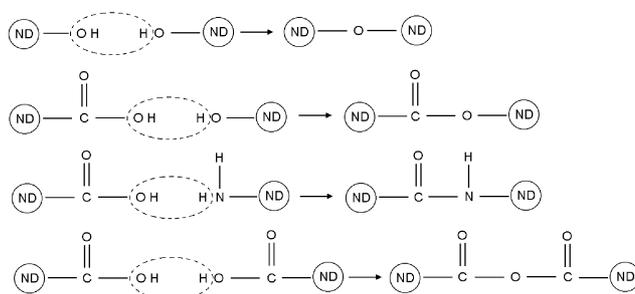


Fig. 5. Schematic representations on the bonding (the forming of C–O–C and C–N–C bonds) between adjacent ND particles.

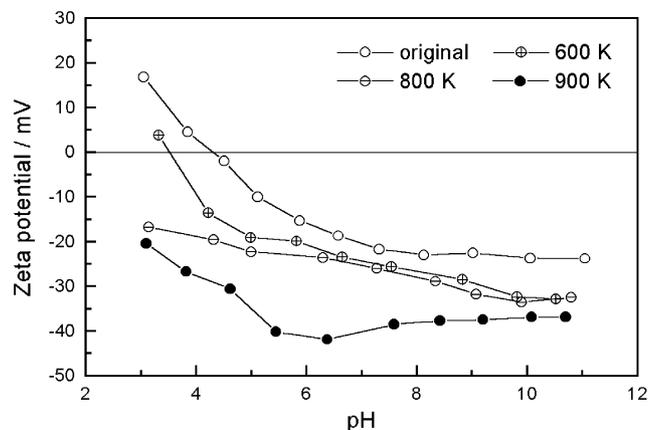


Fig. 6. Influence of heating temperature on surface electrical property: ND surface turns to be more negatively charged along with the increasing of treating temperature.

### 3.4. Surface electrical property

The change of composition of ND surface functional groups in aqueous medium is testified by observing the change of zeta potential (Fig. 6). According to the zeta potential measurement, the original sample is positively charged in acidic medium, the isoelectric point (IEP) of which is located at 4.4. After heating at 600 K, the zeta-pH curve shift downward, and the IEP of which locate at 3.3. Further descending of zeta-pH curve was observed with the heating temperature of 800 and 900 K. No IEP was observed amid these two circumstances, ND particles were negatively charged in the whole observed pH range. This phenomenon testified the composition change of surface functional groups. As oxidation of some surface groups such as hydrocarbon groups, the relative amount and density of carboxyl on ND surface increases. It can be supposed that as there is a large amount of carboxyl groups formed on the ND surface at high temperature, ND particles can be strongly negatively charged in the whole observed pH range, even in acidic environment.

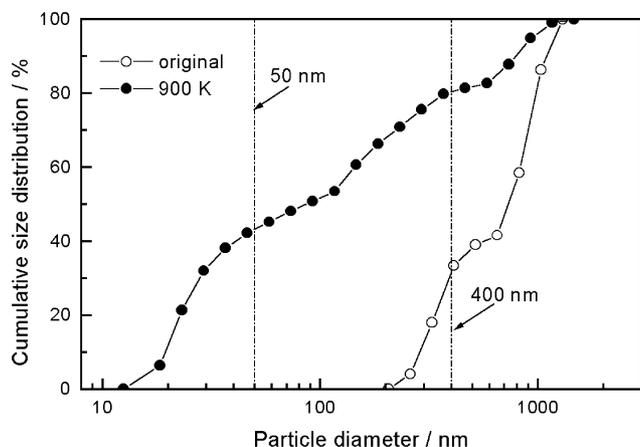


Fig. 7. Cumulative size distribution of original and treated ND samples (in aqueous suspensions, pH: 7).

### 3.5. Dispersion in aqueous medium

Fig. 7 shows the dispersion behavior of original ND and ND sample heated at 900 K in aqueous system at pH 7. As the agglomeration exists, particle diameter of the original sample is coarse but the distribution comparatively narrow. Particles are between 200 and 1000 nm in dimension. After heat-treatment, a portion of small particles in the treated sample increased markedly, as over 40% of the particles are smaller than 50 nm. The results are consistent with the analysis of ND surface electrical property. As the increased absolute value of zeta potential after heat-treatment ensure the electrostatic repulsion between particles, after ultrasonic agitation, small ND particles can stay stable in the suspension.

But, some coarser particles appeared simultaneously in the suspension. This phenomenon has also been observed when an ND sample was heated in  $N_2$  [28]. The coarsening of the particle size may be caused by the formation of C–O–C and C–N–C bonding between adjacent particles as what has been testified in FTIR analysis, and an increase of heating temperature in a definite range may favor this bonding process.

### 3.6. Dispersion in non-aqueous medium

A similar phenomenon is observed in non-aqueous medium, white oil. Because of the limited ionization effect of functional groups, the contribution of electrostatic stabilization of ND particles in this non-polar solvent is restricted. A diblock polymer was introduced here as dispersant to increase the steric repulsion between adjacent particles. This polymer is a kind of polyelectrolyte as it consists of two parts, a long polyester chain as oil-soluble block and anchoring groups like amidocyanogen.

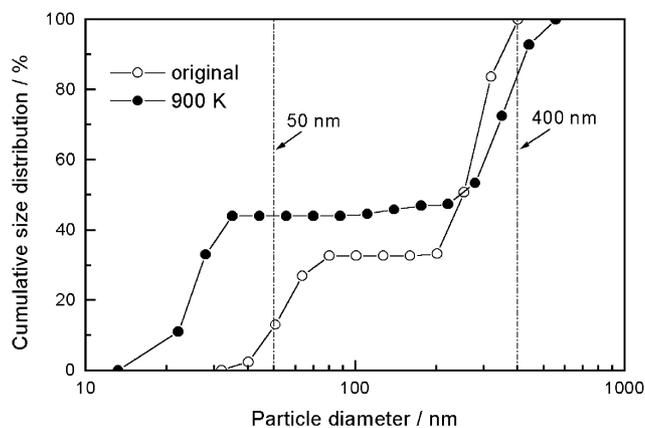


Fig. 8. Cumulative size distribution of original ND and ND after heated at 900 K (in white oil).

The size distributions of ND particles in a non-polar solvent, white oil, are shown in Fig. 8. A portion of small particles increase from 13% of original ND to 44% for the sample treated at 900 K. This may attribute to the intensification of carboxyl groups on ND surface. As there are van der Waals forces and hydrogen bonding between polymer molecular and ND particle, and there also may exist electric attraction between carboxyl groups and the anchoring groups of dispersant, the amount of carboxyl groups on ND surface, which increases along with the heat-treatment temperature, may provide more anchoring points for polymer and the adsorption density of dispersant can thus be increased, consequently, the steric stabilization and the stable suspension of small particles in the solvents can be realized.

## 4. Conclusions

After heat-treatment in air ambient, the formation of more graphite ingredients and obvious oxidation on the ND surface can be observed, while the latter, may impact the surface properties of ND particle greatly. As the oxidation of hydrocarbon groups on ND surface, the density and intensity of carboxyl groups turns to be stronger stepwise correspondingly along with the increase of temperature, which causes ND surface to be more negatively charged in an aqueous system. And as a result of increased electrostatic repulsion between these modified particles, the suspension, after ultrasonic agitation, becomes more stable and create a larger portion of small particles in the suspension.

The formation of ether bonding during heat-treatment may cause the agglomeration of adjacent particles, which may be the reason for the existence of a portion of large aggregates, both in aqueous and non-aqueous media.

A well-dispersed system can also be realized in white oil. For the same reason of the increased carboxyl intensity, the portion of ND with small diameter keeps increasing along with the treating temperature. This may attribute to the attraction between carboxyl groups on ND surface and the diblock polymer dispersant, as the former may provide more anchoring points and facilitate the adsorption of this polyelectrolyte with amidocyanogen as anchoring groups. Meanwhile, the oil-soluble non-polar chain of this polymer dispersant ensures the steric repulsion between particles and, hence, the suspension stability.

### Acknowledgments

Part of this work has been carried out under the financial support by Hunan Provincial Natural Science Foundation of China (Project number: 04JJ3074).

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