A new method for deaggregation of nanodiamond from explosive detonation: graphitization-oxidation method

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In this communication a new method for the deaggregation of detonation nanodiamond (ND) and some preliminary results using this method are presented. ND is firstly graphitized in nitrogen at 1000°C, and then oxidized by air at 450°C to remove the surface graphite layer formed. The sample after such treatment was suspended in water by ultrasonics, and the particle-size distributions were measured. It has been found that the diameters of more than 50% of the ND particles can be reduced to less than 50 nm.

Nanodiamond (ND) prepared by explosive detonation is a unique sort of synthetic diamond. The first papers on this type of diamond were published in 1988 [1,2]. One distinct feature of this kind of diamond is the nanometer-sized particles. As measured by electronic microscopy, the diameters of the fundamental particles are in the range of 4–6 nm [3]. But it can also be seen from the TEM image of ND, a large number of nano-particles aggregate to form fractal clusters with diameters of hundreds of nanometers, or even of several micrometers. But the nature of the aggregation of ND is not very clear. When ND is dispersed in water by ultrasonics, only a small portion of the ND powder can be transferred into particles with diameters less than 100 nm [4].

As accepted by many researches, in nanomaterials there are two kinds of aggregation: that is, the „soft aggregation“ caused by the adsorption of particles, and the „hard aggregation“ caused by chemical bindings between particles. From the HRTEM images of ND [3], it is evident that each nano-sized particle is a diamond single crystallite, which has a unique lattice image, and between two crystallites there is an unclear boundary. We believe that this is, perhaps, a cocrystalline phase between the two crystallites, which causes the aggregation of the particles. We think this is special kind of hard aggregation, which may be stronger than the aggregation caused by the ordinary chemical bindings. Apparently, it is impossible to deaggregate such bonding between diamond crystallites by ordinary chemical methods.

Kuznetsov et al. [5,6] reported that the HRTEM images of ND heat-treated at temperatures higher than 1000°C in vacuum show that graphitization happens on the surface of ND crystallite. We deem that when two diamond crystallites bound together by a co-crystalline is heat-treated, on their surfaces and the boundary regions graphite layers could be formed. If the temperature of heat treatment is not too high and the period of treatment is not too long, it is possible to confine the formation of only a thin layer of graphite on the surface of diamond particles, including their grain boundary. Now if we can use some suitable methods to remove the graphite layer, then the aggregated diamond crystallites, perhaps, can be deagglomerated. We call this method as the graphitization-oxidation method.

ND powders were prepared by the detonation of 50/50 TNT/RDX charge using water as the cooling and protecting medium. The obtained black powder (detonation soot) was treated with a mixture of boiling nitric and sulfuric acid to remove the non-diamond components. For graphitization, the ND was heat-treated in N_2 at 1000°C for 1 h, after which the color of sample changed completely to dark black indicating graphitization occurred. For oxidation, the sample is treated in air at 450°C for several hours. It is worth noticing that only after slight oxidation, i. e., heated in an air flow at 450°C for about 2 h, the black color of the graphitized diamond particles faded and the original color of ND completely recovered. So we can confirm that graphitization of ND at 1000°C for 1 h only produced a thin layer of graphite on the surface of ND crystallites.

The ND sample after the graphitization-oxidation treatment was dispersed in water by ultrasonics. The particle size distributions of ND in the obtained suspensions were measured on a N-4 Plus dynamic laser scattering apparatus (Coutler Co.) and the results are shown in Fig. 1. It can be seen that in the suspension of the ND after graphitization-oxidation treatment, more than 50% of the particles have diameters less than 50 nm (Fig. 1, *b*) which is much more than that in the suspension of the untreated ND (Fig. 1, *a*). So it is believed that the graphitization-oxidation method has some effect on the deaggregation of ND. But it can also be seen that after the graphitization-oxidation treatment some particles with larger diameters (ca 1000 to 2000 nm) are also formed.

The samples were examined by FTIR spectrometry (on a Bio-Rad FTS-165 IR spectrometer). From the spectra (Fig. 2), we can see that after graphitization the characteristic band of carbonyl group ($\nu = 760\,\mathrm{cm}^{-1}$) disappears, and it reappears after oxidation, while the characteristic band ($\nu = 1100\,\mathrm{cm}^{-1}$) of ethereal group (C–O–C) enhanced after graphitization and oxidation, which means that more bridged oxygen bonds are formed. Whether these bridged oxygen bonds are formed on the surfaces of diamond crystallites or between the crystallites is not clear, but we suppose at least a portion of such bridged oxygen bonds

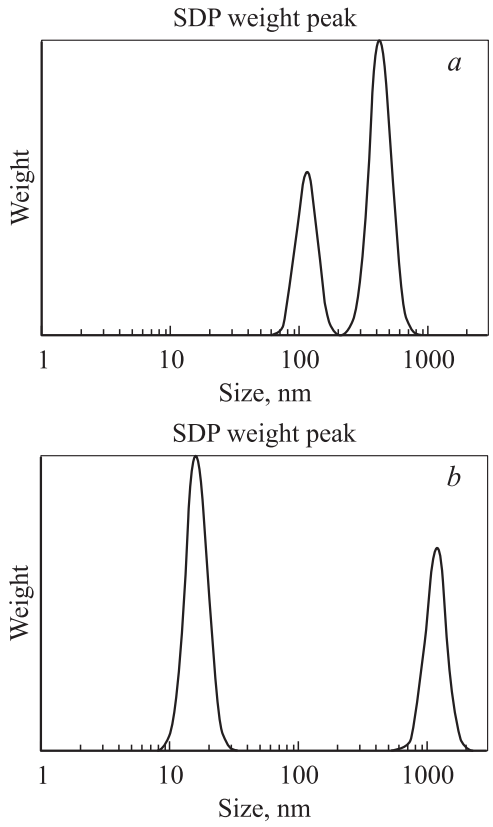

Figure 1. Particle distribution of aqueous suspensions prepared from original ND (*a*) and from ND after graphitization-oxidation treatment (*b*).

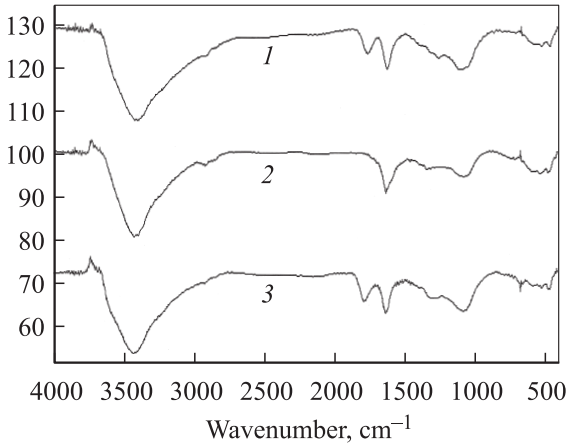

Figure 2. FTIR spectra of original ND (*1*), ND after graphitization (*2*), and sample *2* after oxidation (*3*).

are formed between the diamond crystallites which result in the formation of agglomerates with larger diameters. If our above suggestion is correct, it means that during oxidation, more aggregates caused by bridged ethereal bindings are formed. We deem that in order to deaggregate such kind of bonding some suitable chemical reactions must be used to cleavage the inter-particle ethereal bonding. Some preliminary experiments in this aspect were carried out in our laboratory. Several chemical reactions, which are usually used to cleavage organic ethers, were tested for this purpose, and the samples after treatments were examined by a simple method, that is the sample was suspended in water by ultrasonics and the amount of the ultrafine particles (with diameters less than 100 nm) in the aqueous suspensions were determined by the centrifugal sedimentation method. The suspension was centrifuged at a speed of 4000 rpm for 30 min, and the amount of particles remained in the suspension was determined by weighing the residue after drying. The preliminary results indicate that, among many chemicals used, hydroiodic acid may be the most effective one, after reflexing in HI acid solution for 24 h, the amount of ultrafine particles can be remarkably increased. These experiments are continued now and the detailed results will be published later.

In summary, a new method for the deaggregation of detonation ND is developed. In this method the ND is first heat-treated to set off surface graphitization, and then air oxidation is used to remove the thin surface graphite layer. So this method is called as the graphitization-oxidation method. The preliminary experimental results of deaggregation of ND using this method indicate that it has some positive effects on the deaggregation of ND. Since the graphitization-oxidation process is rather complicated, further investigation is needed to verify the mechanism and usefulness of this method.

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