

1B13. Effect of Hydrothermal Treatment on the Structure and Electronic Properties of Nanodiamond

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Chemical modification of the surface of nanodiamond (ND) particles is expected to give diamond-based functionalized electronic systems. The surface of ND particles as prepared is subjected to structural reconstruction, which results in producing graphitic composites on the surface. Therefore, removing the surface graphitic composites is the requisite for chemical modification. In this study, hydrothermal (HT) treatment in supercritical water is carried out for the purpose of hydrogen termination of the ND surface, and their structural and electronic properties are investigated by means of XRD, SAXS (small angle X-ray scattering), HRTEM, FTIR and Raman spectroscopies, ESR and magnetic susceptibility measurements.

ND samples prepared by detonation techniques and purified by different oxidizing agents were used as starting material ND particles were sealed with distilled water (in the mole ratio of ND:H₂O = 1:3) in a gold capsules and treated at 650°C and 100 MPa during 6, 12, 24 and 36 h. After HT treatment all the samples were dried and annealed in vacuum at 200°C during 12 hours. One sample (6 h HT treated) was additionally annealed in vacuum condition at 700°C during 4 hours.

HRTEM and XRD data show that in the as-received ND sample the scattering objects are diamond grains of ca.4.4 nm in size, with a narrow distribution of the mean diameter. In this case the structure of ND can be described in terms of fractal geometry [1]. The SAXS results suggests that pristine ND is characterized as a scatterer with a size of $L=6.8$ nm and fractal dimension $D=2.5$. The theory of SAXS states that in the case of bulk uniform particles D is equal to 3. Therefore, the deviation from $D=3$ can be explained by fractal-like structure of the ND shell. And the apparent difference in size between scatterer (6.8 nm) and diamond core (4.4 nm) can be attributed to different electronic density distributions, i.e., different degrees of looseness of the fractal shell and diamond core. Indeed, from the definition of fractal dimension $D_1/D_2 \sim \ln L_2/\ln L_1$, where index 1 refers to bulk core with $D=3$, and index 2 refers to scatterer with $D=2.5$. After HT treatment scatterer size L and D depend strongly on treatment time as summarized in Figs. 1a and 1b, respectively. In an earlier stage of HT treatment (12h) the scatterer has $L=5.8$ nm and $D=2.85$, which correspond to the particles with the surface exhibiting a sharper relief. And the scatterer left after the long time HT treatment (24 h) consists of only the diamond core because its size is $L=4.4$ nm and $D=2.93$. The difference of the fractal dimension $D=2.93$ from $D=3$ indicates a weakly pronounced surface relief. By this model, the decrease of scatterer size L and the increase of D with the treatment time increasing are associated with dissolution of shell covering diamond core under HT condition.

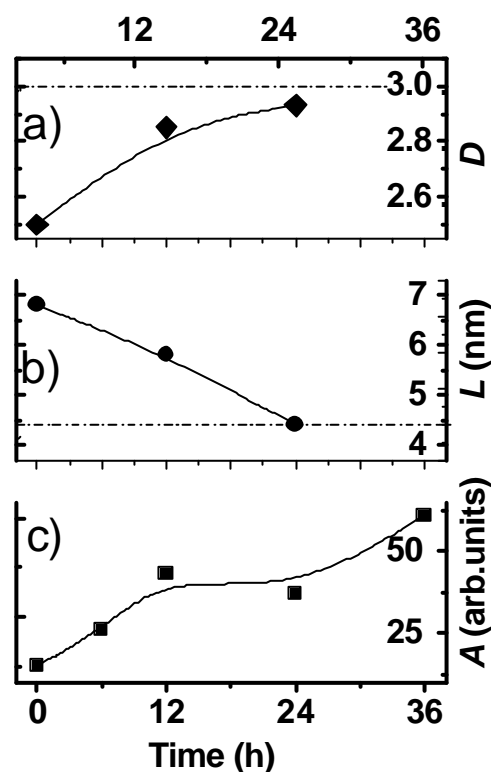


Fig.1. The HT treatment time dependence of the fractal dimension D (a), scatterer size L (b) and the area of the total absorption band A in the C-H stretching region at 2800 - 3000 cm^{-1} (c). Dot-dash lines for $D=3$ and $L=4.4$ nm are the guides for the eyes.

Fig.2 shows FTIR spectra for the as-received ND samples as well as those after HT treatment during 36h at 650°C in supercritical water. The starting sample exhibits a broad absorption bands in the 1000-1500 cm^{-1} and 3400 cm^{-1} regions (last not shown), a strong band with overlapping peaks at 1650 cm^{-1} and 1750 cm^{-1} and weaker bands at 2850, 2920 and 2960 cm^{-1} (Fig.2.a). The major features are retained in the spectrum of ND treated in supercritical water at 650°C (Fig.2.b), but an increase in the intensity in the C-H stretching region at 2800 - 3000 cm^{-1} and the disappearance of the strong band ca. 1750 cm^{-1} are observed. Similarly, the band between 1100 and 1500 cm^{-1} has developed into a broad band near 1100 cm^{-1} and band with peaks at 1260, 1340 cm^{-1} and the shoulder at 1460 cm^{-1} .

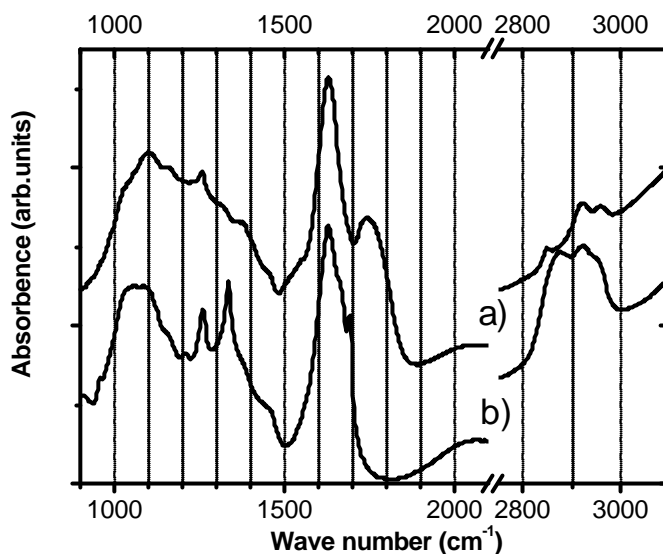


Fig.2. FT IR spectra of ND before (a) and after (b) treatment in supercritical water during 36 hours.

The most characteristic features of the samples purified by different oxidizing agents are displayed in the absorbances around 1750 cm^{-1} . Taking into the account the instability the 1750 cm^{-1} band which disappears after 6 h HT treatment at 650°C this band is assigned to type of carbonyl groups not strong bonded [2].

The band at ca 1000-1150 cm^{-1} has been assigned to C-O stretches in ether-type structures as well as to OH bending modes in water [2]. There are a little change in the absorption intensity of this band and 3400 and 1630 cm^{-1} bands, which are attributed to bending mode of hydroxyl group of water, after 700°C treated; consequently heating cannot remove all the physically adsorbed water. The 1260 cm^{-1} peak is assigned to C-O stretches in thermally stable epoxy structure. A certain amount of various secondary amide carbonyl groups (1260, 1650, 1680 cm^{-1}) also occur in well purified ND [2].

The sharp band at 1340 cm^{-1} , which becomes more distinct after HT treatment, has been observed in the spectra of all diamond materials [2], and has been assigned to C-C stretching vibrations of the diamond lattice interacting with impurities or structural defects. The appearance of this peak and the vanishing of the C=O band near 1750 cm^{-1} at the same time indicate the reduction of the surface carbonyl groups to hydrocarbon species under HT treatment. The similar effect has found for ND sample after H_2 treatment at 800°C for 4 hours [2].

The increase of the intensities of modes in the C-H stretching region at 2800 - 3000 cm^{-1} and the appearance of the shoulder 1460 cm^{-1} also indicate the formation of surface hydrocarbon species. The investigated intensity of the absorption near 2900 cm^{-1} can be related to the hydrogen content on the surface. Fig 1c gives the evolution of the area of the total absorption band (A) in the C-H stretching region at 2800 - 3000 cm^{-1} as a function of treatment time. It shows an increase in A and therefore in the number of C-H bonds as the treatment time increases.

According to the above results, dissolution of surfaces is strongly preferred by hydrothermal treatment and bare ND cluster is produced. The reduction of some surface groups to hydrocarbon species under HT treatment is revealed. The fact that no significant graphitization of diamond surface is found indicates the possibility of HT formation of ND with surface saturated by hydrogen atoms.

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