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Surface modification of nanodiamond in aqueous medium①

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Abstract: The methods of chemical-mechanical treatments (CMT) were utilized for surface modification of nanodiamond in aqueous medium, and a considerably stable suspension system was thus obtained. The size of all the particles in the provided system was less than 100 nm with a narrow distribution and excellent stability, and no obvious change of particle crystal structure after the treatments was observed. The mechanism of the treatments was also discussed. The results show that, because of mechanical treatment effect, addition of ionic surfactants and inorganic regulators, the ζ-potential of nanodiamond shifts upwards during the treatments, and the composition of surface functional groups changes. Carboxyl and hydroxyl groups are intensified after the surface modification, which may contribute to the improvement of dispersion and stability. Meanwhile, the addition of non-ionic polymer can also benefit the suspension stability.

Key words: nanodiamond; surface modification; aqueous medium; CMT
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1 INTRODUCTION

The research and practice of nanodiamond (diamond of nano-scale, in some articles ultrafine diamond (UFD) or ultradispersed diamond (UDD) is called) synthesis has started both in the United States and the former USSR in earlier 1980s[1,2]. After that, reports about the research and synthesis of this nano-scale material present themselves continuously. The products of this kind come forth in Japan, Germany, Great Britain and France as well[3,4]. Scientists inland have also shown their interest and intensive studies have also been conducted[5,6]. This material produced by explosive detonation possesses the properties of both diamond (synthesized by traditional technology) and nano-scale particles[7,8], and thus has a great potential to be put into use as additive of lubricating oil[9,10] and electrochemical or composite plating[11]. And it can also be used in the fields of low-field electron mission[12], antigen delivery vehicles[13], polishing compositions and so forth[14].

Owing to the high specific surface energy, nano-scale particles stay in a thermodynamically unstable state, and thus have a tendency to form aggregate easily, which causes a difficult problem in dispersion and becomes a bottleneck in the application. For nanodiamond, this problem is also quite serious. Since the beginning of its synthesis research, the investigation on its dispersion has been carried out synchronously[15-17]. But up till now, the results could not be regarded as satisfying. The particles in all media in these researches have a mean size of over 300 nm with an unsatisfactory stability.

The dispersion of nanodiamond in aqueous medium is studied in this paper utilizing the method of chemical-mechanical treatment (CMT).

2 EXPERIMENTAL

2.1 Sample

Nanodiamond raw material sample investigated in this paper was a purified product of nanometer-sized diamond synthesized by explosive detonation. It had a specific surface of 293.6 m^2/g, density of $3.05 \times 10^3 - 3.3 \times 10^3$ kg/m^3 and volume resistivity of 7.7×10^7 Ω·cm.

According to the results of X-ray photoelectron energy spectroscopy (XPS), the major chemical elements on the surface of nanodiamond sample are C, O and N, which take 90.65%, 8.09% and 1.14% respectively. And there exists also a little amount of S and Cl.

2.2 Apparatus and methods

X-ray diffracto-spectrometer/Kratky small angle scattering goniometer(SAXS), Zetasizer3000HS and Atomic Force Microscope(AFM) were adopted for size distribution measurement. And Zetasizer3000HS was used to measure the surface ζ-potential as well.

The crystal structures were studied using X-ray diffractometer(XRD) D/max-rA, and infrared spec-

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tra were obtained using the standard technique of KBr-pellet with Nexus 470.

3 RESULTS

Fig. 1 shows the size distribution of nanodiamond sample measured by using SAXS. The particles have a dimension smaller than 60 nm, and the average size is 12 nm.

But when this kind of material was added into water, obvious aggregation and sediment were observed. Using Zetasizer3000HS to test the size of nanodiamond particles in water, as shown in curve (a) in Fig. 2, the size distribution takes a quite large range, and the mean size of particles is 2 359. 1 nm, while no more than 6% particles are smaller than 100 nm. So, it is necessary to promote a surface modification to achieve the stable dispersion of nanodiamond particles in aqueous medium. Chemical-mechanical treatments(The course can be divided into two steps, which can be named as CMT1 for chemical treatment and CMT2 for mechanical treatment, accordingly) were taken in this surface decorating process. While mechanic forces are introduced to crush the aggregate, surfactants and inorganic electrolytes were added to modify the newly created surface. Through this way, an instant surface coating can increase the electrostatic repulsion among particles and improve the hydrophilicity.

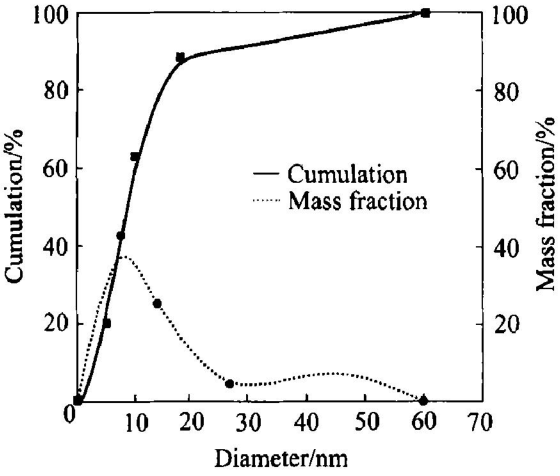

Fig. 1 SAXS analysis of nanodiamond original size

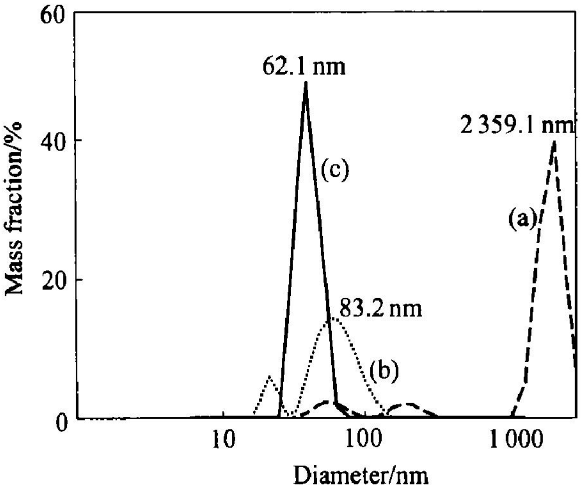

Fig. 2 Size distribution during CMT treatments

The size distribution of nanodiamond after the treatments is shown as curve(b) in Fig. 2, which indicates the actualization of a significant reduction of particle mean size. All the particles within the suspension system are less than 150 nm. Then, after a procedure of classification, a product containing nanodiamond of small size and narrow distribution can be obtained. As shown as curve(c) in Fig. 2, the particle size distributes from 35 nm to 100 nm with the mean value of 62. 1 nm.

The product size is also examined using AFM (Fig. 3). It testified the small-size and dimensional uniformity of nanodiamond particles, while all the particles in the observed visual field are smaller than 100 nm with an even shape and size.

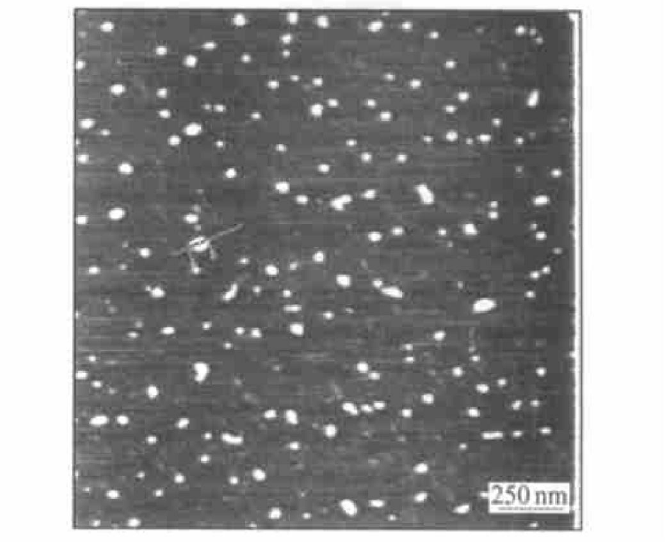

Fig. 3 AFM image of treated nanodiamond

4 DISCUSSION

4. 1 XRD analysis

XRD patterns(Fig. 4) were investigated to check the quality of nanodiamond after these CMT processes. It can be concluded that there is no obvious change of particle crystal structure. In the scan angle 2θ range of 20°– 90°, typical intense diffraction lines of diamond were observed in both the samples before and after CMT processes with 2θ angles of 44° and 76°, which agree well with the crystal faces of {111} and {220} respectively.

4. 2 Surface electric property

Fig. 5 shows the alteration of nanodiamond surface electric property during these processes. Curve 1 reflects the relationship between surface ζ-potential of the raw particles and the pH value of the aqueous medium; while curves 2 and 3 represent the ζ — pH curves of nanodiamond after CMT 1

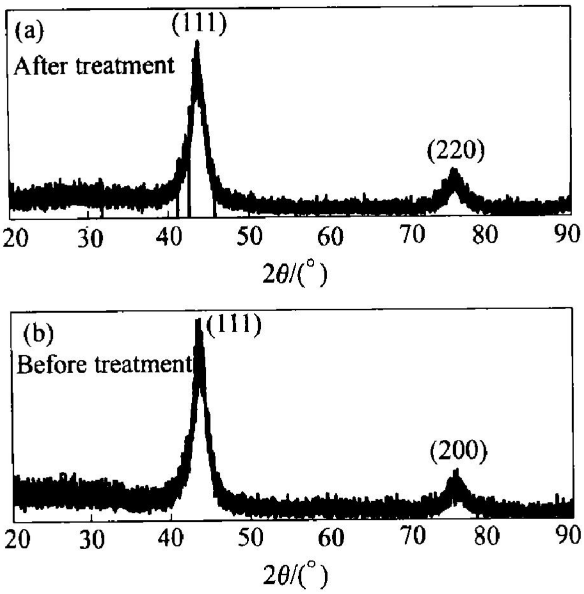

Fig. 4 XRD patterns of samples before and after treatment

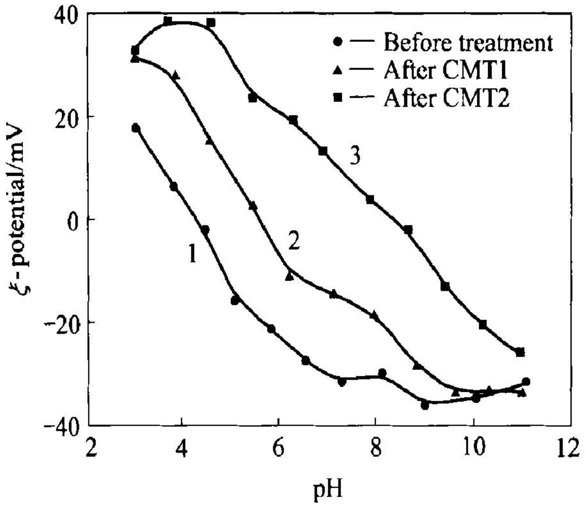

Fig. 5 Surface electric property of nanodiamond

and CMT2, respectively. It can be found that as cationic surfactants are added and the processes are carried through in a light acidic medium, the ζ—pH curve moves stepwise upwards, and the isoelectric point (IEP) moves from 4.3 towards right to 5.6 and 8.4. After these treatments, the surface of nanodiamond particles are positively charged with electricity in a wide range of pH value, of which a considerable high absolute value of ζ-potential can be achieved while pH value of the medium is located from 3 to 5. And a relatively stable dispersion can thus be realized.

The influence of non-ionic surfactants has also been studied in this paper. A non-ionic polymer (RGN-40 as we called) is introduced to treat the sample after CMT2, and the change of dispersion effect can be observed in Fig. 6. The comparison of curves 1 and 2 exhibits the improvement of suspension stability. The average particle size of the sample obtained directly after CMT2 treatment (curve (1)) climbs slowly during the observation period (50 d); while that of another sample (curve (2)), in which the non-ionic surfactant added, almost remains unchanged (pH value of the system is adjusted to be 3.5, and concentration of RGN-40 is 1×10^{-4} mol/L). It can be detected through curve (3) that there is no significant contribution of this non-ionic polymer to surface electric property. The ζ-potential of nanodiamond keeps relatively invariable only with the exception of a slight decrease at higher RGN-40 concentrations.

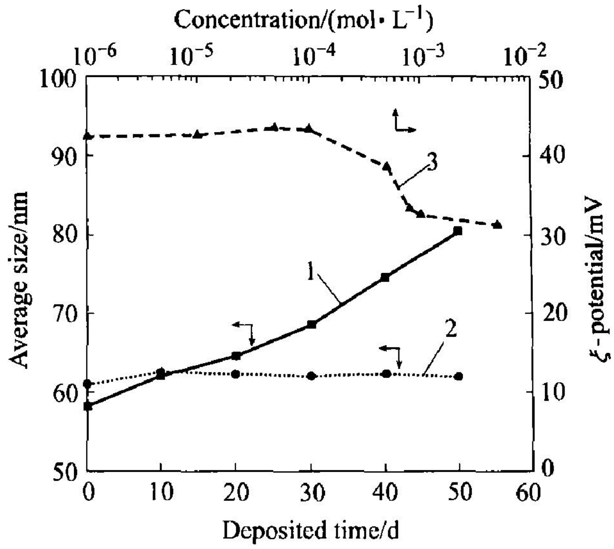

Fig. 6 Influence of non-ionic surfactant

4.3 IR analysis

IR-spectrum of raw nanodiamond sample (Fig. 7(a)) consists of a broad adsorption band with a peak of 3433.76 cm^{-1} (stretching O—H and N—H vibration), adsorption band with the peak of 1 764.89 cm^{-1} (stretching C═O vibration in carbonyl, carboxyl groups) and adsorption band with the peak of 1 629.29 cm^{-1} (deformation NH vibration). In addition, adsorption bands of stretching C—H vibrations are observed in the area with the peaks of 2 923.16 cm^{-1} and 2 855.02 cm^{-1} (representing asymmetric and symmetric vibration, correspondingly). The broad adsorption band with the peak at 1 117.43 cm^{-1} may correlate with the stretching C—OH vibration of hydroxyl groups and stretching C—O vibration of carboxyl groups. And the purification methods of the nanodiamond production may have influence on the surface groups, for example peaks of 1 117.43 cm^{-1} and 619.74 cm^{-1} may also be attributed to the existence of SO_4^-, ClO_4^-, as the results of purification using sulphuric or perchloric acid.

After the treatment of CMT1 (Fig. 7(b)), an obvious change of spectrum is the disappearance of adsorption band of stretching C ═ O vibration of carbonyl, carboxyl groups, which is substituted by

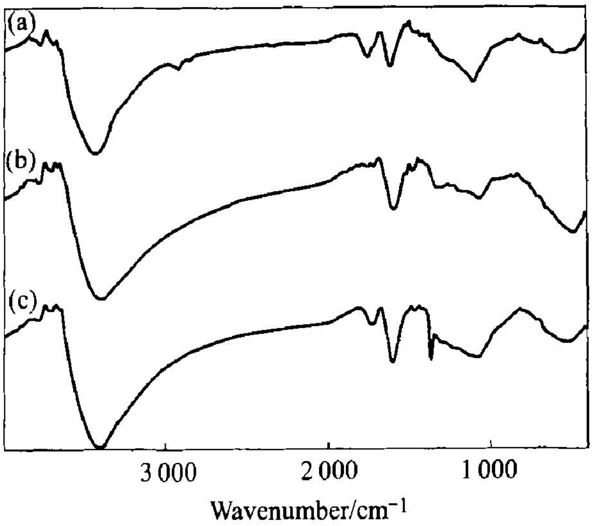

Fig. 7 IR spectra of CMT processes

adsorption bands of carboxylic acid anions with the peaks of 1 611.74 cm^{-1} and 1 324.48 cm^{-1} (asymmetric and symmetric vibration, respectively). This may be due to the transformation of carboxyl groups to carboxylate during the CMT1 process. Another phenomenon is that the peaks of stretching O—H, N—H vibration (3 433.76 cm^{-1}), stretching C—OH vibration of hydroxyl groups and stretching C—O vibration of carboxyl groups (1 117.43 cm^{-1}) move towards lower wave numbers, to 3 405.94 cm^{-1} and 1 087.29 cm^{-1} respectively, which may be on account of the bonding between functional groups like hydroxide, carboxyl and amine and groups of surfactants during surface modification.

Adsorption bands of carboxylic acid anions disappear after CMT2 treatment, and the adsorption band of carbonyl, carboxyl groups present itself again (Fig. 7(c), 1 756.42 cm^{-1}). This may attribute to the adjustment of aqueous medium, while the carboxylate is decomposed and the hydrolysis and ionization of carboxyl groups are restricted. The adsorption bands of 1 622.12 cm^{-1} and 1 382.19 cm^{-1} indicate the adsorption of the added surfactants and inorganic electrolytes on the surface of nanodiamond. And with the same reason, the peaks of stretching O—H, N—H vibration, stretching C—OH vibration of hydroxyl groups and stretching C—O vibration of carboxyl groups move towards higher wave numbers, to 3 417.12 cm^{-1} and 1 100.37 cm^{-1} correspondingly. After the treatment, the adsorption of hydrophilic functional groups like carboxyl and hydroxyl are strengthened, which may contribute to the hydrophilicity and stability of particles.

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