



Effect of laser pulse parameters on the size and fluorescence of nanodiamonds formed upon pulsed-laser irradiation

Peikang Bai^b, Shengliang Hu^{a,b,*}, Taiping Zhang^c, Jing Sun^c, Shirui Cao^b

^a Key Laboratory of Instrumentation Science & Dynamic Measurement (North University of China), Ministry of Education, National Key Laboratory Science and Technology on Electronic Test and Measurement, Taiyuan 030051, PR China

^b School of Materials Science and Engineering, North University of China, Taiyuan 030051, PR China

^c School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:

Received 30 June 2009

Received in revised form 1 March 2010

Accepted 15 March 2010

Available online 20 March 2010

Keywords:

A. Optical materials

B. Laser deposition

D. Crystal structure

D. Luminescence

ABSTRACT

The size of nanodiamonds formed upon laser irradiation could be easily controlled over simply adjusting laser pulse parameters. The stable size and structure of nanodiamonds were mostly determined by laser power density and pulse width. Both large nanodiamonds with multiply twinning structure (MTS) and small nanodiamonds with single crystalline structure (SCS) emitted strong visible light after surface passivation, and their fluorescence quantum yield (QY) was 4.6% and 7.1%, respectively.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The chemical, optical and electrical properties of nanoparticles strongly depend on their size, shape, and crystal structure [1–3]. It is a major scientific breakthrough that people can systematically manipulate the size and crystal structure of carbon nanoparticles, such as nanodiamond which is attractive for using as the polishing material, seeding treatment of the substrate in CVD film growth, etc. [1–4]. In these applications, homogeneous distribution size and good dispersion obviously are key factors. Furthermore, the light emission from carbon nanoparticles with surface passivation, such as diamond and graphite structure, is size-dependent, i.e., the smaller the size of carbon nanoparticles are, the higher their photoluminescence (PL) efficiency they have [5–10]. Fluorescent diamond and other carbon-based nanoparticles are highly promising in biology and medicine as fluorescent probes because they are biocompatible, chemically inert, and low cytotoxic [5–17]. Therefore, many researchers expect that an available method can be found to produce fluorescent carbon nanoparticles with homogeneous size and crystalline structure to help them to

understand the luminescent mechanism and improve the PL quantum efficiency [7,8,11–13].

Nowadays, nanodiamond is generally produced from carbon contained in explosives by their detonation [18–20]. Although this method yields nanodiamonds with a narrow distribution of particle sizes centered around 5 nm, the disadvantages of aggregation and impurities in these nanodiamonds retard their applications to a large extent [18–20]. Based on the high temperature and high pressure (HTHP) produced by high-power laser, a new avenue that pulsed-laser irradiates graphite target or powder in liquid has been opened to synthesize nanodiamonds [21–26]. Importantly, the experiment results show that the size of nanodiamond is possibly determined by the laser parameters. For example, large nanodiamonds (above 30 nm) tend to be synthesized by ns-pulsed laser with high-power density [21–23], while small nanodiamonds (below 15 nm) are produced by ms-pulsed laser with low-power density [24–26]. Therefore, we proposed that the size of diamond or other nanoparticles can be controlled over simply adjusting the laser parameters. A general method for obtaining homogeneous sized nanoparticles is the addition of some organic reagents which inhibit the growth of nanoparticles under laser irradiation [27], but there are some disadvantages, for example, the introduction of impurities in nanoparticles or difficulty in removing the organic molecular from nanoparticle surfaces. Hereby, we expect to control the size of nanoparticles by adjusting laser parameters when nanoparticles are prepared by pulsed-laser irradiation in liquid.

* Corresponding author at: School of Materials Science and Engineering, North University of China, Xueyuan Road No. 3, Taiyuan 030051, PR China.

Tel.: +86 351 3557423; fax: +86 351 3557519.

E-mail address: hsliang@yeah.net (S. Hu).

Nanodiamonds have been synthesized successfully by irradiating graphite suspension using millisecond-pulsed laser in the previous work [24–26]. In the present work, we firstly report that the parameters of pulsed laser affect the size distribution of nanodiamonds produced by laser irradiation, which can be used for regulating fluorescent properties of nanodiamonds.

2. Experimental

Commercial natural graphite powders that are supplied by Qingdao Taineng Graphite Co., Ltd. of China with a purity of 99.97% and a particle size less than 2 μm are used as precursors. Graphite powders were mixed with water, and then the water suspension was irradiated by a Nd:YAG pulsed-laser with a wavelength of 1.06 μm . The pulse width (pulse duration) of the laser can be tuned from 0.1 ms to 20 ms in 0.1 ms increment. The repetition frequency of 20 Hz and laser power density of $4 \times 10^6 \text{ W cm}^{-2}$ were used during the irradiation of graphite suspension. The power densities were adjusted by controlling the distance between the focusing lens and the liquid surface and the values were measured by a laser power meter (LEM 2020). Sample A and B were prepared at the pulse width of 0.4 and 1.2 ms, respectively. After 4 h irradiation, both samples were purified by boiling in perchloric acid to remove the untreated graphite. The as-prepared nanodiamonds suspended in water are colorless.

Although various organic molecules or polymers can be used as surface-modified solvent, polyethylene glycol (PEG) is not only aqueous compatible and nontoxic but also readily conjugated with antibodies or other bioactive molecules. We attempted many types of PEG with different molecular weight and other polymers as surface-modified solvent to investigate their impact on the PL of diamond nanoparticles, but in the present paper we take PEG_{200N} as an example.

PEG_{200N} of 250 mg was mixed with the purified samples A and B. The mixture was heated to 120 $^\circ\text{C}$, held for 72 h, and then cooled down to the room temperature. After such treatments, the color of samples A and B is changed from colorless to brownish-yellow. The PL spectra of two samples were measured on a Hitachi F4500 fluorescence spectrophotometer under excitation at the wavelength of 420 nm. FEI Tecnai G² F20 field-emission-gun transmission electron microscopy (TEM) was employed to analyze the size and structure of diamond nanoparticles.

3. Results and discussion

Samples A and B were obtained under the pulse width with 0.4 and 1.2 ms, respectively, while other laser parameters are invariable. TEM examination shows that the diamond nanocrystals (DC) in sample B range from 2 to 13 nm in diameter and that there are two dominant groups with diameters of about 4 and 7.5 nm, respectively. The microstructure of the DC was extensively investigated by high-resolution TEM (HRTEM). The HRTEM images indicate that nanotwinning configurations exist in most of the DC (~98%) with diameters larger than 4 nm. The twinning structures include single twins, double twins, and multiple twins. However, for sample A only single crystals are observed and their size distribution mostly range from 3 to 4 nm. To give a reliable size distribution of the different DC structures, we recorded more than 210 nanocrystals and carried out a statistical analysis, as shown in Fig. 1.

Compared with the results obtained by ns-pulsed laser with high-power density, the higher yield around 1% is gotten besides the smaller size in the present experiment. However, the yield gotten by our method is still lower than that by detonation method. It should be noted that the crystalline structure changes from single crystal to multiple twins with the size of the DC

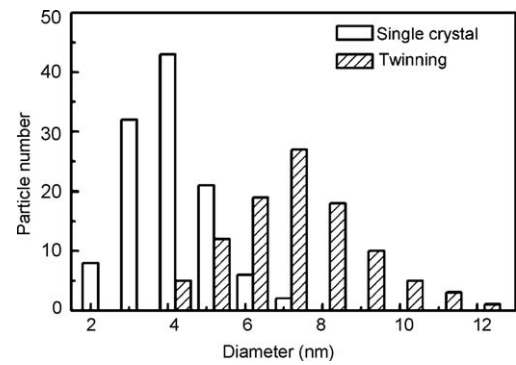


Fig. 1. Size distribution of both single crystals and multiple twins.

increase based on Fig. 1. In order to control the size of the DC by laser parameters, the reasons for the formation of smaller DC and the size-dependent structure must be figured out.

The reason that the smaller DC are obtained in our experiment results from the conditions produced by ms-pulsed laser irradiation, which may determine the stability of diamond nucleation and the diamond nucleus growth. Based on the nanothermodynamical theory reported by Yang et al. [21,28], the Gibbs free energy is expressed as a function of the radius r , pressure P , and temperature T under the assumptions of spherical and quasi-isotropic nanocrystals.

$$\Delta G(r, P, T) = \frac{4}{3}\pi r^3 \frac{\Delta g}{V_m} + 4\pi r^2 \gamma \quad (1)$$

where V_m , Δg , γ represent the molar volume, the molar-volume Gibbs free energy, and the surface energy, respectively. When the conditions are around the equilibrium line, Δg is determined by [28]:

$$\Delta g = \Delta V \times \Delta P \quad (2)$$

where ΔV is the mole volume difference between diamond and graphite. According to the thermodynamic phase diagram of carbon, the phase equilibrium line function $P(T)$ of the diamond-graphite phase transition in the bulk is approximately expressed by $P^e = 2.01 \times 10^6 T + 2.02 \times 10^9$ [21,28,29]. On the other hand, the nanoseize-induced additional pressure is given by the Laplace-Yong equation, as $P^n = 2\gamma/r$. So the phase equilibrium line on the nanometer scale is a function of the temperature, pressure and nanocrystal radius, and is expressed by $P^{ne} = 2.01 \times 10^6 T + 2.02 \times 10^9 - 2\gamma/r$. Therefore, for the formation of the DC [21,28]:

$$\Delta g_d = \Delta V \left(P - 2.01 \times 10^6 T + 2.02 \times 10^9 + \frac{2\gamma_d}{r} \right) \quad (2a)$$

For the formation of the graphite nanocrystals (GC) [29]:

$$\Delta g_g = \Delta V \left(2.01 \times 10^6 T + 2.02 \times 10^9 - \frac{2\gamma_g}{r} - P \right) \quad (2b)$$

When the phase transition takes place near the size-dependent phase equilibrium line, the Gibbs free energy of between the DC formation and the GC formation is equal, i.e.:

$$\frac{4}{3}\pi r^3 \frac{\Delta g_d}{V_{md}} + 4\pi r^2 \gamma_d = \frac{4}{3}\pi r^3 \frac{\Delta g_g}{V_{mg}} + 4\pi r^2 \gamma_g \quad (3)$$

According to $V_{md} = 3.417 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, $V_{mg} = 5.187 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, and $\gamma_d = 3.7 \text{ J m}^{-2}$, $\gamma_g = 0.55 \text{ J m}^{-2}$ [21,29], the dependence of the critical diameter of the DC formation as a stable phase on pressure is illustrated in Fig. 2 at the given temperature in the range of 4000–4200 K. We can see clearly from Fig. 2 that the

Download English Version:

<https://daneshyari.com/en/article/1491157>

Download Persian Version:

<https://daneshyari.com/article/1491157>

[Daneshyari.com](https://daneshyari.com)