

Available online at www.sciencedirect.com**SciVerse ScienceDirect**

Procedia Engineering 32 (2012) 1054 – 1060

**Procedia
Engineering**www.elsevier.com/locate/procedia

I-SEEC2011

Synthesis of Carbon Particles using Laser Ablation in Ethanol

V. Thongpool^a, P. Asanithi^{a*}, P. Limsuwan^{a,b}^a*Applied Nanotechnology Laboratory (ANT Lab), Department of Physics, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand*^b*Thailand Center of Excellence in Physics, CHE, Ministry of Education, Bangkok 10400, Thailand***Elsevier use only:** Received 30 September 2011; Revised 10 November 2011; Accepted 25 November 2011.

Abstract

Carbon particles were synthesized via laser ablation of a bulk graphite in ethanol medium using Nd:YAG laser with a wavelength of 1064 nm. The target was irradiated by the laser beam with a pulse energy of 3 J, a pulse repetition rate of 2 Hz, and a pulse duration of 5 ms. Effect of using ethanol as a liquid medium for laser ablation on physical, chemical, and optical properties of resulted carbon particles was reported. SEM images presented that a flake-like morphology of graphite in the target has been transformed into a flower-like cluster after the ablation. Raman measurement showed that G peak position of the graphite flakes and that of the synthesized carbon particles were similar, about 1582 cm⁻¹, whereas D peak position and its shape of the synthesized particles was different from those of graphite flakes. UV-visible and fluorescent spectrometers were used to investigate absorption and emission characteristics of the particles, respectively. The carbon particles can absorb a light in the UV range and emit a photoluminescence of bright blue-green color.

© 2010 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of I-SEEC2011

Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/4.0/).*Keywords:* Carbon particles; Laser ablation; Graphite flake; Fluorescence

1. Introduction

In the past few years, developments in nanotechnology have significantly promoted the discovery of a new carbon allotrope at a nanometer scale such as nanofiber, nanodiamond, and carbon nano-onion [1]. Carbon related-nanomaterials have attracted much attention from various branches of up-to-date research because of their unique optical, mechanical and electrical properties [2-3]. They also could have a profound impact on many applications such as catalysis support, oil adsorbent [3], drug delivery,

* Corresponding author. Tel.: +662-470-8860; fax: +662-872-5254.

E-mail address: asanithi@hotmail.com

hydrogen storage, junction device, and sensor [4]. Various techniques have been employed for synthesizing carbon nanostructure, e.g., arc discharge in protection gases, microwave plasma, chemical vapor deposition and supersonic cluster beam deposition [5, 6]. However, all of these methods are difficult and time consuming.

Pulsed laser ablation of the target in liquid could offer a simple way of synthesizing carbon nanomaterials. When the laser beam is focused the target settled in the liquid, the target surface at the focal point has been heated, melted, vaporized, and ionized to generate plasma, respectively. The plasma plume is formed with a unique feature depending on temperature and pressure [7, 8]. Another advantage of using pulsed laser ablation in liquid medium is its low-cost process comparable to the vacuum equipment. Moreover, the easiness of gathering the resulted particles after synthesis is also represented a strong point of using laser ablation in liquid. The nanoparticles are suspended in the liquid medium, instead of fuming in the air. It has been reported that laser ablation in liquid is very useful for synthesizing various kinds of nanomaterials such as metal oxide [9, 10, 11], silver [12], gold [13], and semiconductor [14].

In this study, carbon particles were synthesized via laser ablation of graphite target in ethanol. Effect of ethanol medium on physical, chemical, and optical properties of the synthesized carbon particles was reported. The physical and chemical properties of the particles were characterized by scanning electron microscope (SEM), Raman spectroscopy, UV-visible spectrometer, and fluorescent spectrometer. The carbon particles exhibit a bright fluorescence that may be useful for optoelectronics and chemical sensing. Compared with Ray *et al.* [15], the synthesized process is easier and faster. Particularly, raw materials and liquid medium of this study are inexpensive.

2. Experimental

The experimental procedure is illustrated by Fig. 1. The graphite target is located at the bottom of a glass vessel, filled with ethanol solvent until the solvent is 0.5 cm above the target. The target was ablated using Nd:YAG laser (MIYACHI : ML-2331B), focused by a 5 cm focal-length plano-convex lens on the surface of graphite target. Laser energies employed in this study was 3.0 J/pulse. Pulse repetition rate and pulse duration were 2 Hz and 5 ms, respectively. After 5,000 pulses of laser ablation, the suspension (without the target) was again irradiated with the laser beam for 25,000 pulses, while the suspension was kept stirring using magnetic bar. After the ablation, the suspension was centrifuged at 12,000 rpm for 60 minutes to remove the large size particles. UV-visible (Jasco, V570) and fluorescent spectrometers (Hitachi, F2500) were used for study the optical properties of the carbon particles dispersed in ethanol. The morphological features of dried carbon particles were investigated by a scanning electron microscopy (Hitachi, S4700) and Raman spectroscopy.

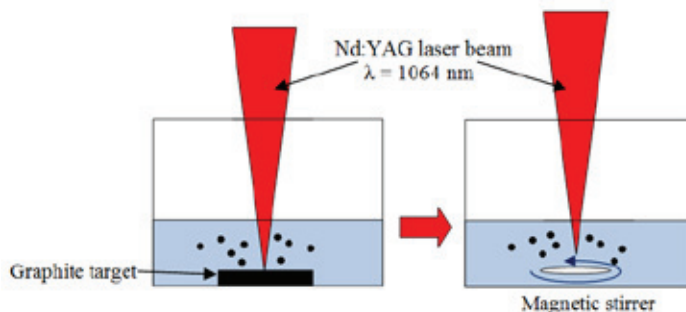


Fig. 1. Experimental setup for synthesizing carbon nanoparticles

3. Results and discussion

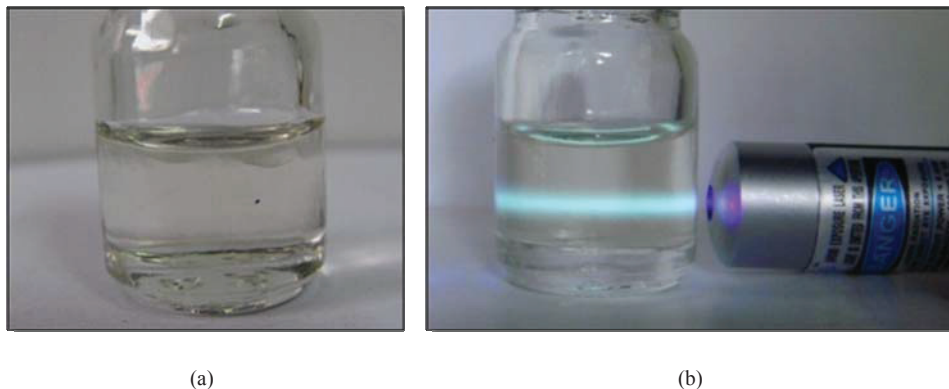


Fig. 2. Photographs of carbon nanoparticles dispersed in ethanol (a) after ablation and (b) when excited with 405 nm laser beam

After ablation, the suspension turns to light brown color as shown in Fig. 2(a). The suspension exhibits bright blue-green fluorescence when irradiated with UV light of 405 nm (Fig. 2 (b)). To prepare the sample for SEM, the suspension was dropped on a silicon surface for three times to have enough particles. Fig. 3(a) shows SEM image of raw graphite powder used as a target. The morphology was flake-like shape with a size of more than 5 μm . Fig. 3 (b) shows SEM image of the carbon particles. The synthesized carbon particles (CP) have a broad size distribution ranging from 200-500 nm (Fig.4) with strongly aggregation into a flower-like cluster. The aggregation of the particles may be due to multiple drops of the suspension on silicon surface (after the first drop dried, the next drop was added), which is in agreement with Ray *et al.* [15].

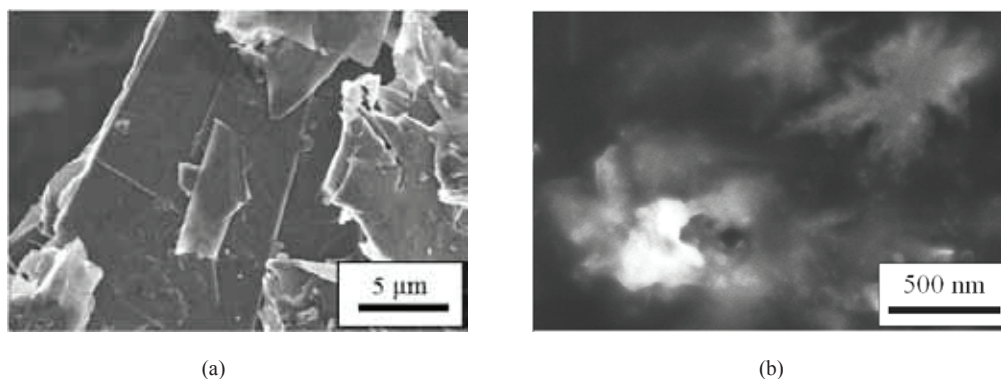


Fig. 3. SEM images of (a) graphite flake before synthesized and (b) carbon particles after synthesized

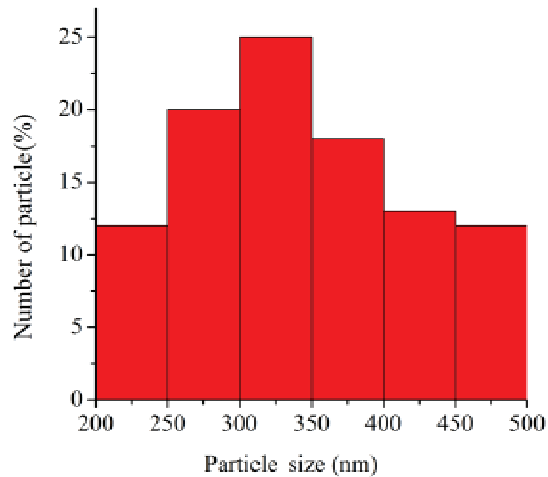


Fig. 4. Size distribution of the synthesized carbon particles

The vibrational properties of the raw graphite target and the synthesized carbon particles were measured by Raman spectroscopy. Fig.5 shows Raman spectra of graphite powder (black line) and the synthesized carbon particles (red dot line). Raman spectrum of graphite powder exhibits two dominant peaks at around 1362 cm^{-1} and around 1582 cm^{-1} , corresponding to the disorder band (D band) and graphitic band (G band) [16]. Similarly, Raman spectrum of the synthesized particles shows two prominent peaks at around 1350 cm^{-1} and 1582 cm^{-1} . D peak position and its shape of the synthesized particles were slightly different from those of graphite flakes, which may be results from a change in the graphite morphology.



Fig. 5. The Raman spectra of graphite and synthesized carbon particles

Fig. 6 shows the UV-visible spectrum of synthesized carbon particles dispersed in ethanol. The absorption spectrum was due to the electronic transitions [17]. The synthesized carbon particles represent

the absorption peak at about 325 nm as shown in Fig.6. This absorption may be contributed from the $\pi \rightarrow \pi^*$ electronic transition of C=C. The position is slightly different from the $\pi \rightarrow \pi^*$ transition normally found in the carbon which is in a range of 180 - 280 nm [17]. The shift to longer wavelength may be resulted from the ethanol molecules absorbed on the surface of carbon particles which may generate the $\pi - \pi$ interaction between the imidazolium rings of the ionic solvent and carbon particles [18].

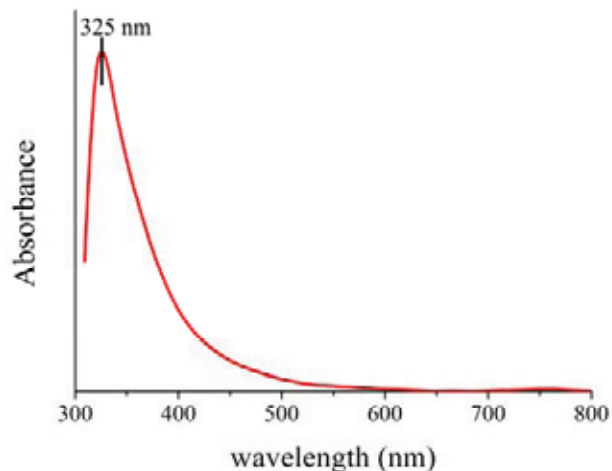


Fig. 6. The absorption spectra of carbon particles in ethanol

The photoluminescent spectra of the synthesized carbon particles in ethanol were studied using different excitation wavelengths, including 350, 400, and 450 nm. The emission peaks shift to longer wavelength when increasing the excitation wavelength. The maximum intensity of fluorescent emission was obtained from the excitation wavelength of 350 nm as shown in Fig.7. Using this excitation wavelength yields the emission peak with the full width half max (FWHM) at about 400 - 500 nm, which is correlated with the bright blue-green fluorescence as shown in Fig. 2 (b).

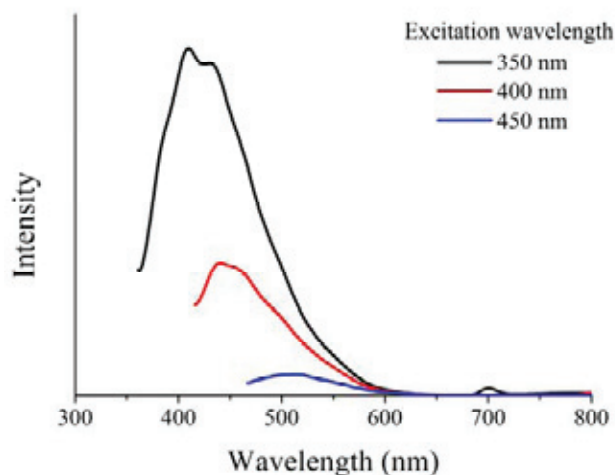


Fig. 7. Photoluminescent spectra of carbon particles dispersed in ethanol. Three different excitation wavelengths were presents

4. Conclusion

In summary, carbon particles with fluorescent property have been successfully synthesized by laser ablation of graphite target in ethanol. SEM images presented a flower-like morphology of the particles with a broad size distribution ranging from 200-500 nm. Raman measurement shows that G peak position of the synthesized particles was similar to those of the raw graphite. D peak position and its shape were slightly different from those of the raw graphite, which may be resulted from a change in the graphitic characteristics of the synthesized carbon particles. The synthesized carbon particles can absorb light in the UV region and emit bright blue-green color, which may be very useful for several applications, such as optoelectronics, chemical sensors, medical imaging.

Acknowledgements

This work had partially been supported by Thailand Center of Excellent in Physics (ThEP) and King Mongkut's University of Technology Thonburi under The National Research University Project.

References

- [1] Tian L., Ghosh D. *et al.* Nanosized Carbon Particles from Natural Gas Soot. *Chem. Mater* 2009; **21**:2803-2809.
- [2] Gao XH, Cui YY, Levenson RM *et al.* In vivo Cancer Targeting and Imaging with Semiconductor Quantum Dots. *Nat Biotechnol* 2004; **22(8)**:969-976.
- [3] Li Z. F and Ruckenstein E.. Water-Soluble Poly(acrylic acid) Grafted Luminescent Silicon Nanoparticles and Their Use as Fluorescent Biological Staining Labels. *Nano Letters* 2004; **4(8)**: 1463–1467.
- [4] Chen C., Sun X., Jiang X. *et al.* A Two-Step Hydrothermal Synthesis Approach to Monodispersed Colloidal Carbon Spheres. *Nanoscale Res Lett* 2009; **4**:971–976.
- [5] Gang X., Shen-li J. and Zong-qian S. The production of carbon nano-materials by arc discharge under water or liquid nitrogen. *New Carbon Materials* 2007; **22(4)**: 337-341.
- [6] Semaltianos N.G., Perrie W., Sharp M. *et al.* Nanoparticle Generation by Femtosecond Laser Ablation. In *ICALEO@ 2007 Congress Proceedings of Nanomanufacturing Conference*. Florida, USA, 114 -118.
- [7] Phouc T.X. and Ruey-Hung C. Synthesis of cation-exchanged laponite suspensions by laser ablation of microsized-metal particles in liquid. *Optics and Lasers in engineering* 2011; **49**: 396-402.
- [8] Sasaki K. and Takada N. Liquid-phase laser ablation. *Pure Appl. Chem* 2010; **82**:1317-1327.
- [9] Tsuji T. *et al.* Laser ablation of cobalt and cobalt oxides in liquids: influence of solvent on composition of prepared nanoparticles. *Applied Surface Science* 2005; **243(1-4)** : 214-219.
- [10] Acacia N. *et al.* Laser ablation synthesis of indium oxide nanoparticles in water. *Applied Surface Science* 2010; **256(22)**: 6918-6922.
- [11] Barreca F. *et al.* Small size TiO₂ nanoparticles prepared by laser ablation in water. *Applied Surface Science* 2010; **256(21)**: 6408-6412.
- [12] Ganeev R.A. *et al.* Characterization of optical and nonlinear optical properties of silver nanoparticles prepared by laser ablation in various liquids. *Optics Communications* 2004; **240(4-6)**: 437-448.
- [13] Kim H.J, Bang I.C. and Onoe J. Characteristic stability of bare Au-water nanofluids fabricated by pulsed laser ablation in liquids. *Optic and Laser in Engineering* 2009; **47(5)**: 235-238.
- [14] Lalayan A.A. Formation of colloidal GaAs and CdS quantum dots by laser ablation in liquid media. *Applied Surface Science* 2005; **248(1-4)**: 209-212.
- [15] Ray S.C. *et al.* Fluorescent carbon nanoparticle: synthesis, characterization and bio-imaging application. *The Journal of Physical Chemistry C* 2009; **113(43)**: 18546-18551.
- [16] Zhang S. *et al.* Raman and peels studies of magnetron sputtered a-C. *International Journal of Modern Physics B* 2000; **14(2-3)**: 268-273.
- [17] Russo C. *et al.* The characteristics of soot formed in premixed flames by different fuels. *Chemical engineering Transactions* 2010; **22**: 41-46.
- [18] Wei Y. *et al.* Carbon nanoparticle ionic liquid hybrids and their photoluminescence properties. *Journal of colloid and interface science* 2011; **358**: 146-150.