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## Pulsed Laser Ablation of Graphite Target in Dimethylformamide

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### Abstract

Carbon nanoparticles were synthesized using laser ablation of a graphite target in dimethylformamide (DMF) using Nd:YAG laser with a wavelength of 1064 nm. The target was irradiated by the laser beam with a pulsed energy of 3 J, a pulsed repetition rate of 2 Hz and a pulsed duration of 5 ms. SEM images presented that a flake-like morphology of graphites in the target transformed into a spherical-like shape with a broad size distribution ranging from 80-130 nm. The Raman spectrum showed the structure of graphite was changed after laser ablation. UV-visible and fluorescent spectrometers were used to investigate absorption and emission characteristics of the carbon nanoparticles, respectively. The fluorescent carbon nanoparticles which ablated in DMF can absorb a light in the UV range and emit a fluorescence of bright blue-green color.

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## 1. Introduction

Carbon nanomaterials have become popular fields for researcher since they have been widely used in many areas such as catalysis supports [1-3], gas adsorbents [4], drug delivery [5], hydrogen storage [6], junction device [7], and sensor [8]. Various methods have been used to synthesize carbon nanomaterials, e.g., arc discharge [9], microwave plasma [10], chemical vapor deposition [11] and laser ablation [12]. Among them, laser ablation is a widespread method for synthesis of nanoparticles that can be synthesized in gas, vacuum or liquid. Pulsed laser ablation in liquid was first reported by Patil and co-worker in 1987 [13]. In this method, solid target is immersed in a liquid medium and the laser beam is focused through the liquid onto the target surface. The advantage of this method is simple and does not require a vacuum system. The controllability of particle size is shown to be dependent upon operating conditions (wavelength, laser power, pulsed duration, etc.).

This paper reports the synthesis of carbon nanoparticles using laser ablation of graphite via a long pulsed laser in dimethylformamide (DMF). The morphology, graphitic nature, absorption and fluorescence of carbon nanoparticles are also reported.

## 2. Experimental

### 2.1. Preparation

The experimental procedure is illustrated in Fig. 1. Graphite target was obtained from pressing graphite micropowders under an isobaric. The consolidation pressure was 200 bars. In Fig. 2 graphite target is placed at the bottom of a glass vessel, filled with DMF until its level was approximately 0.5 cm above the target. The target was then ablated using Nd:YAG laser (MIYACHI : ML-2331B), focused by a 5 cm focal-length plano-convex lens on the surface of the graphite target.

Laser energy 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 target was removed and the black suspension was again ablated with the laser beam for 25,000 pulses, while the suspension was kept stirring using magnetic bar.

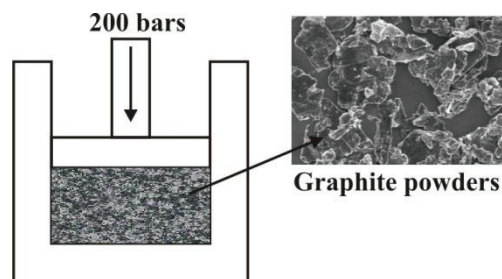


Fig. 1. Schematic of graphite powder consolidation process

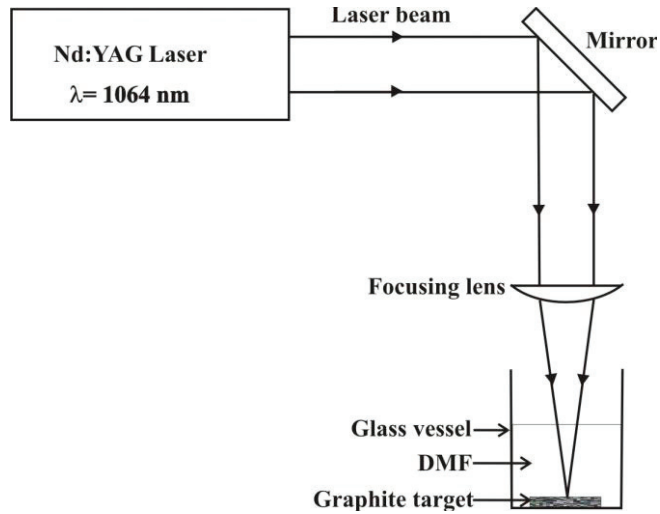


Fig. 2 Schematic of the experimental setup

## 2.2. Characterization

After ablation, the morphological features of carbon nanoparticles were investigated by scanning electron microscope (SEM) and Raman spectroscopy. To prepare sample for SEM and Raman spectroscopy, the carbon nanoparticles suspended in DMF were dropped on a silicon wafer for three times to have enough particles and dry in air for one day. Moreover, UV-visible (Jasco, V570) and fluorescent spectrometers (Hitachi, F2500) were used for study the optical properties of the carbon particles suspended in DMF.

## 3. Results and discussion

Fig. 3(a) shows SEM image of graphite target. The Flake-like shape with a size more than  $5 \mu\text{m}$  was observed.

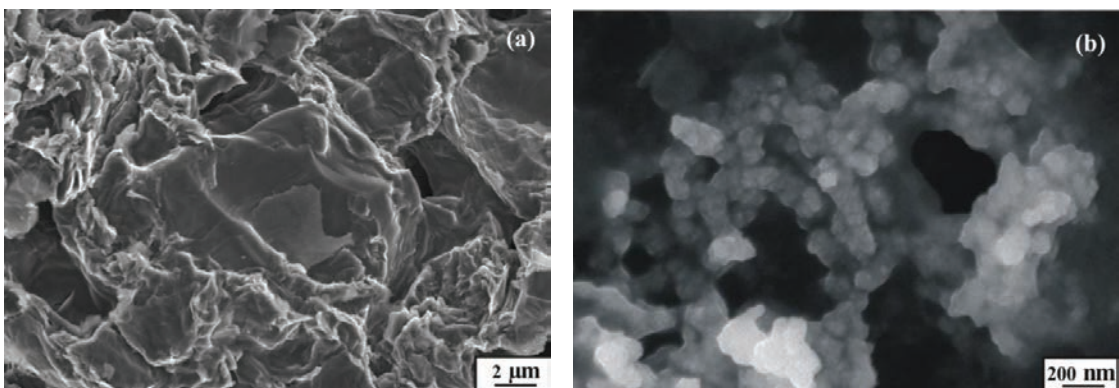


Fig.3 SEM images of (a) graphite powders and (b) carbon nanoparticles

During ablation, the surface of graphite target was evaporated by the laser light. It induced plasma plume on the surface of the graphite target. The plasma plume was expanded, condensed and generated carbon nanoparticles. The properties of nanoparticle such as structure, morphology and size depend on laser parameter and nature of liquid medium. Fig. 3(b) shows SEM image of synthesized carbon nanoparticles with a broad size distribution ranging from 80-130 nm (Fig. 4).

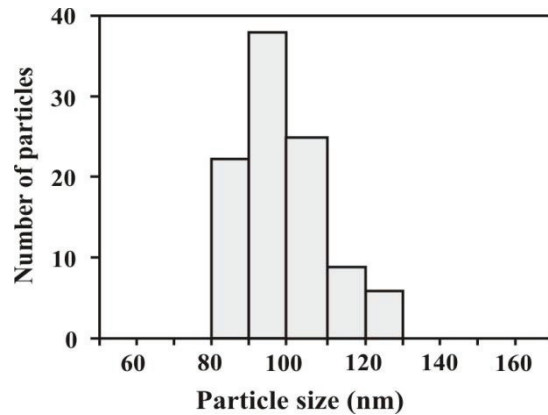


Fig. 4 Size distribution of the synthesized carbon nanoparticles

The Raman spectrum corresponding to the synthesized carbon nanoparticles is presented in Fig. 5. The curve was fitted with Gaussian – Lorentzian functions. It represents D peak at  $1373\text{ cm}^{-1}$  and G peak at  $1582\text{ cm}^{-1}$ . Typically, Graphite shows single peak at  $1580\text{ cm}^{-1}$  (G peak), which is consistent with the carbon-carbon stretching mode [14]. When graphite is changed to disordered, a new peak call D peak will occur.

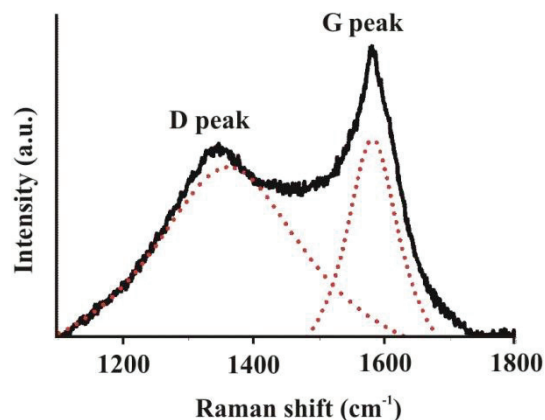


Fig. 5 Raman spectrum of synthesized carbon nanoparticles

UV-visible spectrum of carbon nanoparticles suspended in DMF is displayed in Fig. 6, which shows the absorption peak at 274 nm. The absorption spectra of carbon nanoparticles arised from the electronics transition between  $\pi \rightarrow \pi^*$  states [15].

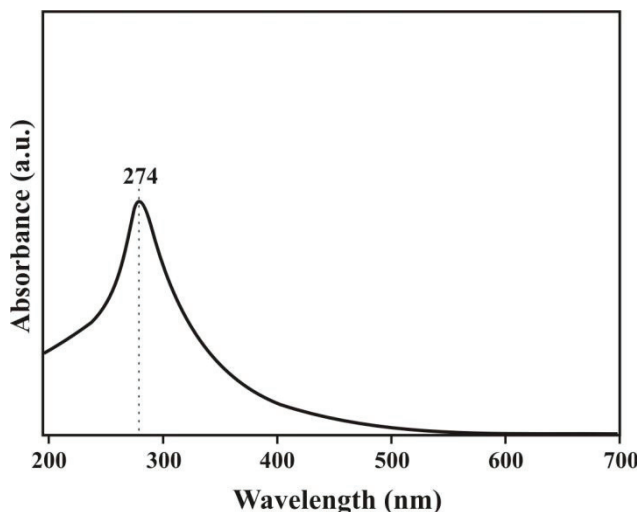


Fig. 6 UV-visible spectrum of synthesized carbon nanoparticles suspended in DMF

In addition, the carbon nanoparticles suspended in DMF exhibits bright blue-green fluorescence when irradiated with UV light of 405 nm, which corresponds with our previous report. The fluorescent property of synthesized carbon nanoparticles was confirmed by fluorescent spectra as shown in Fig. 7.

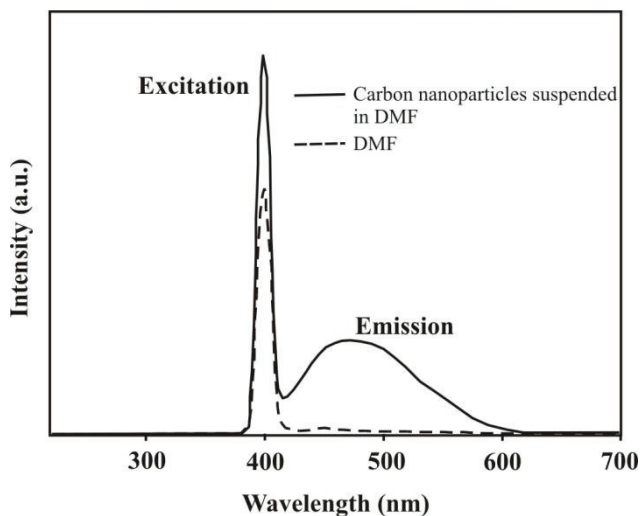


Fig. 7 Fluorescent spectra of carbon nanoparticles suspended in DMF and pure DMF with excitation wavelength of 400 nm

In Fig. 7, the carbon nanoparticles suspended in DMF shows dominant peak at 472 nm when excited with wavelength of 400 nm and pure DMF shows no fluorescence when excited with same wavelength. The results confirmed that the fluorescence caused by the carbon nanoparticles.

To further investigate their fluorescent property, fluorescence of the carbon nanoparticles was studied using different excitation wavelengths. As shown in Fig. 8, the excitation wavelength varied from 350 to 500 nm, the emission peak shows a red – shifted, which may be attributed to the presence of carbon nanoparticles with different sizes in DMF.

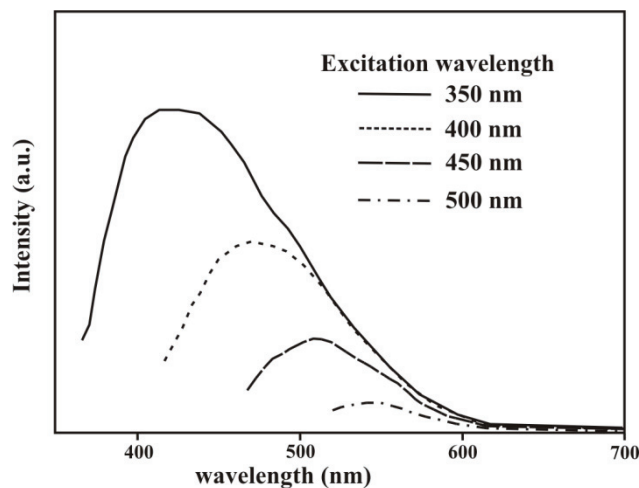


Fig. 8 Fluorescent spectra of carbon nanoparticles suspended in DMF with excitation wavelength of 350, 400, 450 and 500 nm

#### 4. Conclusion

In summary, carbon nanoparticles have been successfully synthesized by laser ablation of graphite target in DMF. SEM images presented a spherical-like shape of the carbon nanoparticles with a broad size distribution ranging from 80-130 nm. Raman measurement shows a change in the graphitic characteristics of the synthesized carbon nanoparticles. The synthesized carbon nanoparticles can absorb light in the UV region and emit bright blue-green color.

#### Acknowledgements

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#### References

- [1] Narayanan, R. and El-Sayed, M.A. Carbon-supported spherical palladium nanoparticles as potential recyclable catalysts for the Suzuki reaction. *J Catal*, 2005; **234**(2), 348-355.
- [2] Liu, Z., Gan, L.M., Hong, L., Chen, W. and Ji Lee, J. Y., Carbon-supported Pt nanoparticles as catalysts for proton exchange membrane fuel cells. *J Power Sources*, 2005; **139**(1-2), 73-78.
- [3] Xu, J., Cao, J., Yu, X., Zou, Z., Akins, D. L., and Yang, H., Enhanced catalytic hydrogen release of  $\text{LiBH}_4$  by carbon-supported Pt nanoparticles. *J Alloy Compd*, 2010; **490**(1-2), 88-92.
- [4] Liao, Q., Sun, J., and Gao, L., Adsorption of chlorophenols by multi-walled carbon nanotubes treated with  $\text{HNO}_3$  and  $\text{NH}_3$ . *Carbon*, 2008; **46**(3), 553-555.
- [5] Oh, W.-K., Yoon, H., and Jang, J., Size control of magnetic carbon nanoparticles for drug delivery. *Biomaterials*, 2010; **31**(6), 1342-1348.
- [6] Yang, C.-C., Li, Y. J., and Chen, W.-H., Electrochemical hydrogen storage behavior of single-walled carbon nanotubes (SWCNTs) coated with Ni nanoparticles. *Int J Hydrogen Energ*, 2010; **35**(6), 2336-2343.
- [7] Jin, Z., Li, X., Zhou, W., Han, Z., Zhang, Y., and Li, Y., Direct growth of carbon nanotube junctions by a two-step chemical vapor deposition. *Chem Phys Lett*, 2006; **432**(1-3), 177-183.

- [8] Quercia, L., Loffredo, F., Alfano, B., Ferrara, V. L., and Francia, G. D., Fabrication and characterization of carbon nanoparticles for polymer based vapor sensors. *Sensor Actuat B-Chem*, 2004; **100(1-2)**, 22-28.
- [9] Sano, N., Formation of multi-shelled carbon nanoparticles by arc discharge in liquid benzene. *Mater Chem Phys*, 2004; **88(2-3)**, 235-238.
- [10] Yu, J., Zhang, Q., Ahn, J., Yoon, S. F., Li, R. Y. J., Gan, B., Chew, K., and Tan, K.H., Synthesis of carbon nanostructures by microwave plasma chemical vapor deposition and their characterization. *Mat Sci Eng B-Solid*. 2002; **90(1-2)**, 16-19.
- [11] Yoon, Y. J., and Baik, H. K., Catalytic growth mechanism of carbon nanofibers through chemical vapor deposition. *Diam Relat Mater*, 2001; **10(3-7)**, 1214-1217.
- [12] Kitazawa, S., Abe, H., and Yamamoto, S., Formation of nanostructured solid-state carbon particles by laser ablation of graphite in isopropyl alcohol. *J Phys Chem Solids*, 2005; **66(2-4)**, 555-559.
- [13] Patil, P.P., Phase, D.M., Kulkarni, S.A., Ghaisas, S.V., Kanetkar, S.M., Ogale, S.B. and Bhide, V.G., Pulsed-laser-induced reactive quenching at liquid-solid interface: Aqueous oxidation of iron, *Phys. Rev. Lett.*, 1987; **58**, 238–241.
- [14] Chen, G.X., Hong, M.H., and Chong, T.C., Preparation of Carbon Nanoparticles with Strong Optical Limiting Properties by Laser Ablation in Water. *J. Appl. Phys.*, 2004; **95(3)**, 1455-1459.
- [15] Jager, C., Henning, T., Schlogl, R. and Spillecke, O., Spectral Properties of Carbon Black. *J non-cryst solids*, 1999; **258**, 161-179.
- [16] Thongpool, V., Asanithi, P., and Limsuwan, P., Synthesis of Carbon Particles using Laser Ablation in Ethanol. *Procedia Engineering*, 2012; **32**, pp. 1054-1060.