Supporting Information

Laser Wavelength Modulated Pulsed Laser Ablation for Selective and Efficient Production of Graphene Quantum Dots

Sukhyun Kang,‡[ab], Jeong Ho Ryu,‡[c] Byoungsoo Lee,[a] Kyung Hwan Jung,[a] Kwang Bo Shim,[b] Hyuksu Han,*[ad] Kang Min Kim*[a]

[a]Korea Institute of Industrial Technology, Gwahakdanji-ro 137-41, Gangwon-do, 25440, Republic of Korea. E-mail: kmkim@kitech.re.kr

[b]Department of Materials Science and Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea.

[c]Department of Materials Science and Engineering, Korea National Uninversity of Transportation 50 Daehak-ro, Chungju-si, Chungbuk 380-702, Republic of Korea

[d]Department of Materials Science and Engineering, Hongik University, Sejong-ro 2639, Sejong, Republic of Korea. E-mail: dducks82@gmail.com

‡These two authors contributed equally to this work.

Corresponding Authors

Department of E-mail: kmkim@kitech.re.kr, dducks82@gmail.com

Experimental section

Materials

MWCNTs were prepared by catalyst chemical vapor deposition (CCVD) method which is purchased by HANWHA chemical (Republic of Korea), and High purity ethanol was purchased from Sigma Aldrich.

Preparation of GQDs and GOQDs

GQDs and GOQDs were prepared by the simple and facile PLE process using MWCNTs in high-purity ethanol. In a typical process, 50 mg of MWCNTs (Hanwha chem, Republic of Korea) was dispersed in 500 ml of ethanol (> 99%, Sigma Aldrich) solutions. Ultrasonication was subsequently performed on the solution of 2 h to achieve a homogeneous dispersion of MWCNTs. 30 ml of solutions was transferred in 30 ml glass vials, and then the PLE process was performed on the fixed vials glass for 10 min using a Q-switch ND:YAG laser system was employed at room temperature and in the air. The MWCNTs suspension was ablated by a horizontal pulsed laser beam (355 nm and 532 nm, third harmonic and second harmonic) at a repetition rate of 10 Hz. The pulsed width was 10 nm, and the ablation energy of 50 mJ. After the PLA treatment, the GQDs and GOQDs suspension was centrifuged at 15000 rpm at 1 hours and were later filtered using syringe filters (Millipore, 0.22 μm pore size). After that, the purified solution were dried over night at 80 ℃.

Characterization of GQDs and GOQDs

HR-TEM images were taken using a 2100F field emission gun TEM (JEM 2100F, JEOL, USA, 200 kV) for GQDs and GOQDs samples. XPS spectra were recorded for both samples using VG ESCALAB 220i (Thermo scientific, USA). XPS survey and high-resolution scans were performed with the pass energies of 100 eV and 20 eV, respectively. X-ray beam size was approximately 100 ㎛. GQDs and GOQDs samples for XPS measurement were prepared via a spin coating technique. Silicon (Si) substrate was used for spin coating. The rotation speed was adjusted to 3,000 rpm. The samples were dried at room temperature for 2 hrs before the measurement. Room temperature PL spectra of GQDs and GOQDs were collected using a photoluminescence spectrophotometer (PerkinElmer, LS55 with 100mW laser diode, USA) in the wavelength range from 400 nm to 700 nm. The excitation wavelength used for measuring PL emission spectra was 430 nm.

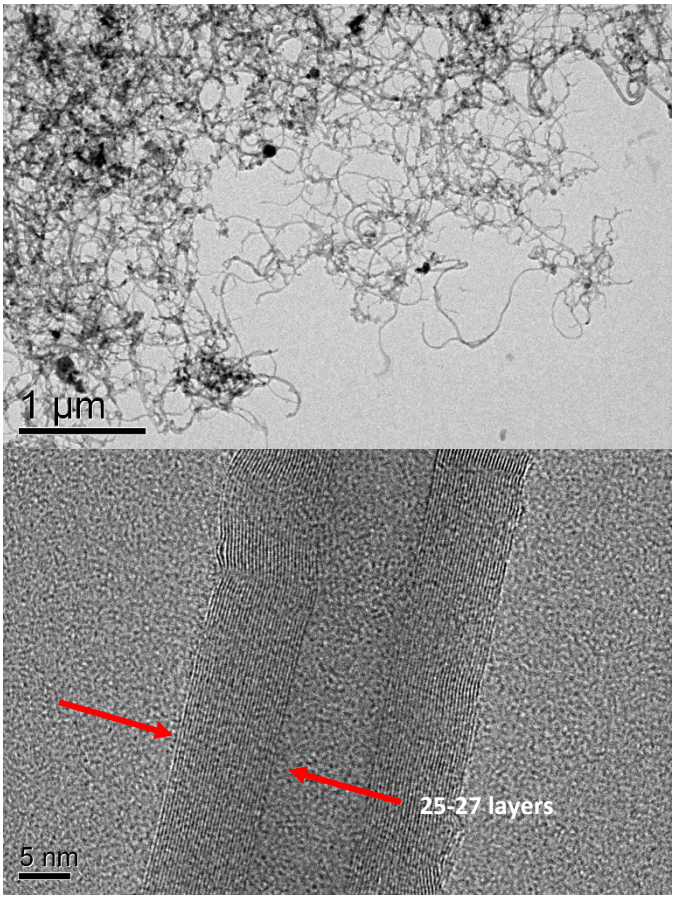


Fig. S1 TEM and HR-TEM images of multiwall carbon nanotube

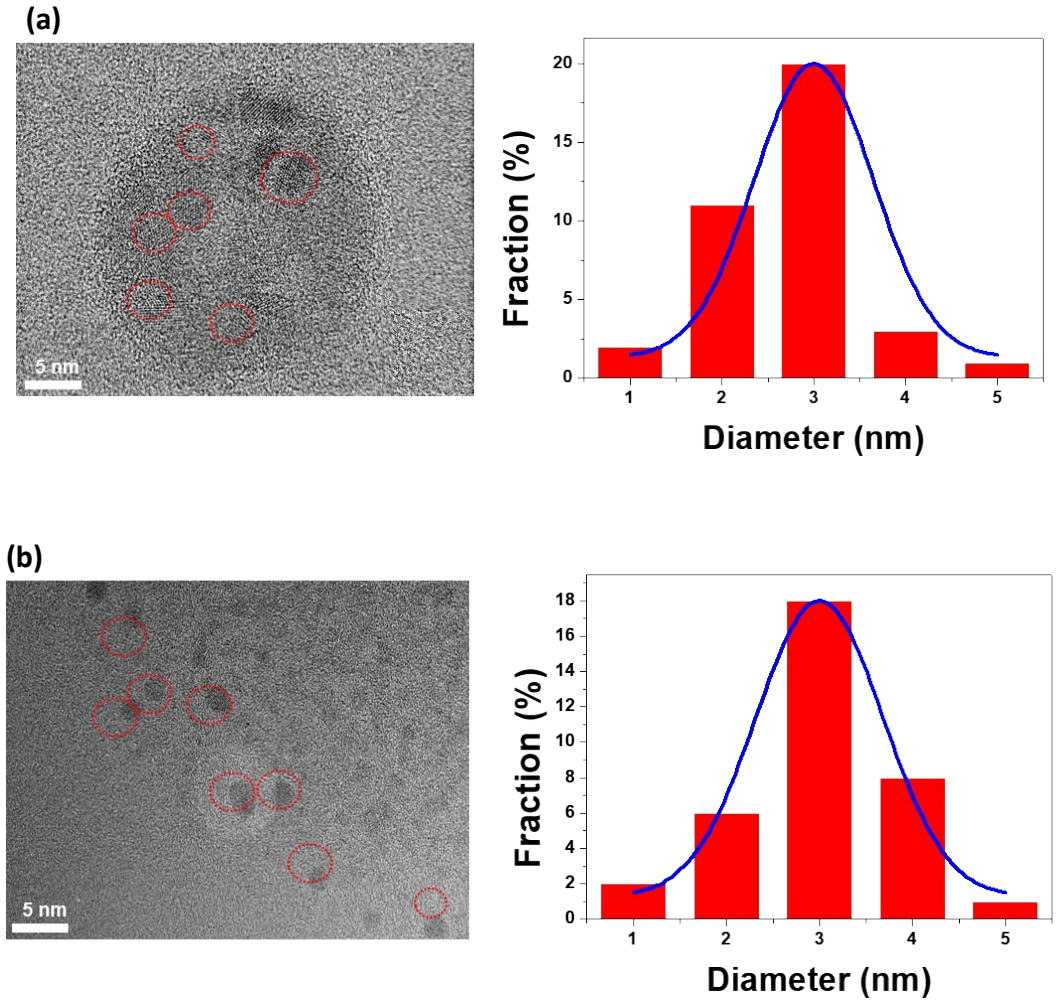


Fig. S2 HR-TEM images and size distribution of (a) GQDs and (b) GOQDs.

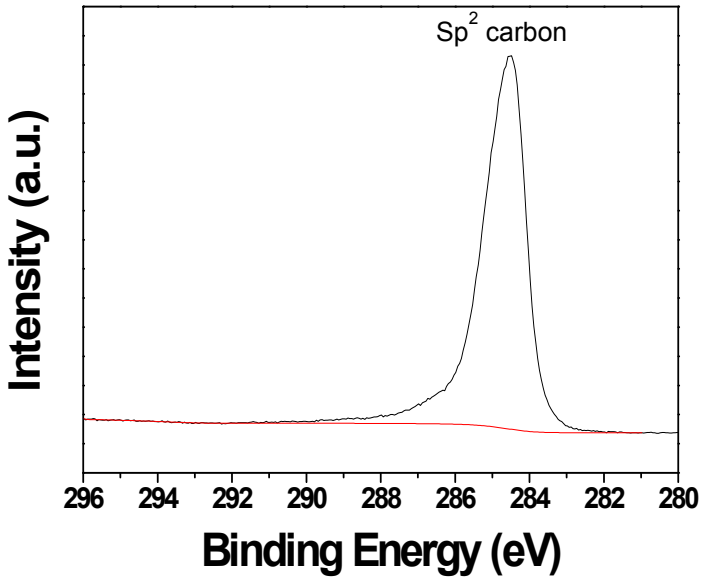
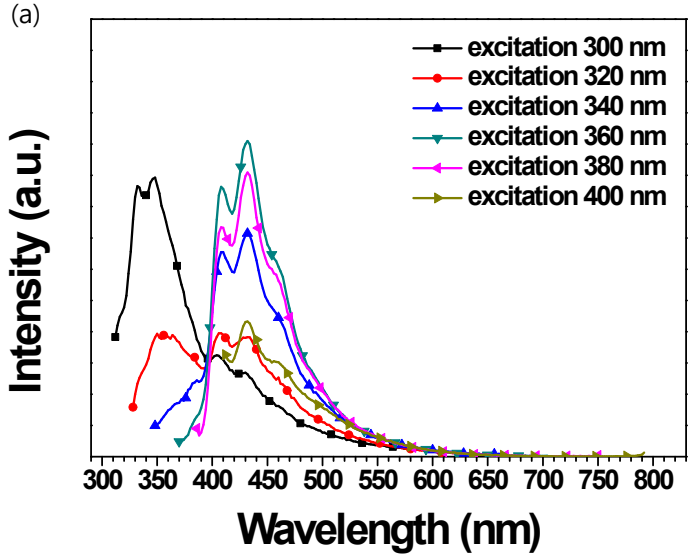


Fig. S3 XPS analysis of MWCNTs

(a)



(b)

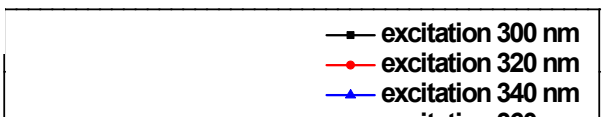


Fig. S4 PL properties of GQDs (a) and GOQDs (b)

Table S1. XPS fraction of GQDs and GOQDs

	Peak Binding Energy (eV)	**GQDs**	**GOQDs**
C=C and C-C (%)	284.4	86.55	55.91
Hydroxyl, Carboxylate group (%)	286-288.6	13.45	44.09