

1 **Supporting Information**

2 **Facile Method to Sort Graphene Quantum Dot by Size through Ammonium Sulfate**

3 **Addition**

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25 **Experimental section**

26 **Synthesis of CMG suspension**

27 CMG was prepared using a modified Hummer's method. Natural graphite (1 g) (SP-1, Bay
28 Carbon, USA) and 40 ml H₂SO₄ (Junsei, Japan) were added to a 250-ml flask at room
29 temperature. The mixture was stirred and cooled to 0°C in an ice bath. Then, 7 g KMnO₄
30 (Sigma Aldrich, Korea) was slowly added to the mixture over 5 minutes with stirring. The
31 temperature of the mixture was brought to 35°C in a water bath and maintained for 2 hours.
32 The reacted mixture was then cooled in an ice bath and diluted by an addition of 200 ml of
33 water. After gas evolution ceased, H₂O₂ (Sigma Aldrich, Korea) was added to the mixture.
34 The GO (Graphene oxide) suspension was filtered through a glass frit filter (medium size)
35 and washed several times with a 10% HCl (Junsei, Japan) solution. Finally, the GO powder
36 was dried in a vacuum at room temperature for 7 days.

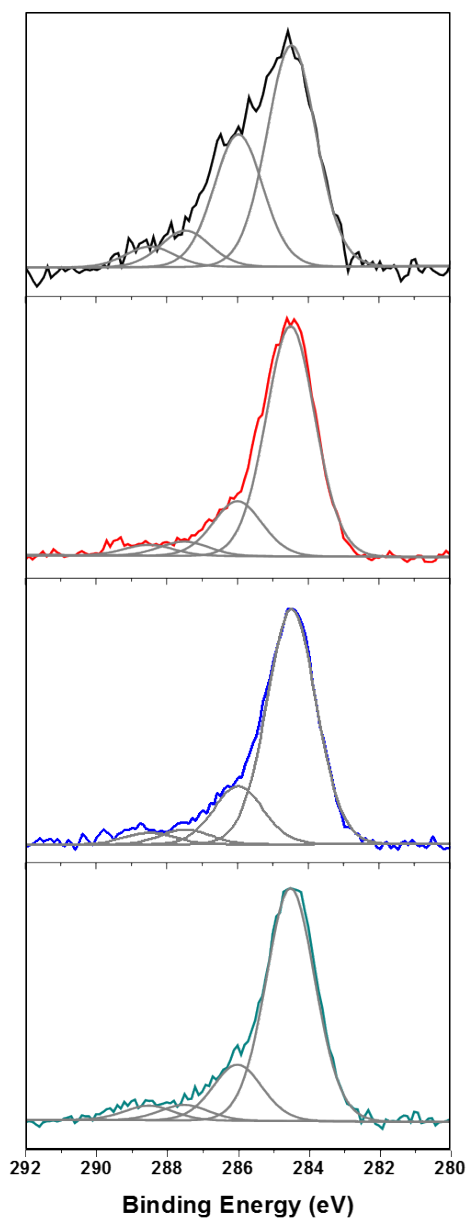
37 **Separation of GQD from the CMG suspension**

38 CMG was prepared using a modified Hummer's method. To prepare the suspension, the as-
39 prepared GO (1 mg/ml) was dispersed in DI water by means of ultrasonication for 30
40 minutes. Prior to the separation process, the agglomerated GO particles were removed by
41 ultracentrifugation at 10,000 rpm for 5 minutes. (NH₄)₂SO₄ was added to raise the
42 concentration of salt to 50 mM, and this was followed by magnetic stirring at 400 rpm for 10
43 minutes. Then, the supernatant were separated from the salted-out precipitates with
44 ultracentrifugation at 10,000 rpm for 5 minutes, as well as the salt were removed by dialysis.
45 The aforementioned process was repeated with 100, 300, and 500 mM (NH₄)₂SO₄.

46 **Characterization**

47 Transmission electron microscopy (Tecnai G F30 S-Twin, FEI, Netherlands) was used to
48 observe the microstructures and sizes of the salted-out GQDs. The sizes of 60 of these
49 prepared specimens were measured using an image analysis technique. The GQD

50 composition in the samples was evaluated by X-ray photoelectron spectroscopy (ESCA 2000,
51 Thermo VG Scientific, UK) and Micro-Raman spectroscopy (LabRAM HR UV/Vis/NIR,
52 Horiba Jobin Yvon, France). A high-resolution micro-photoluminescence system (LabRAM
53 HR UV/Vis/NIR PL, Horiba Jobin Yvon, France) and UV-Vis spectrophotometry (HP 8483,
54 Hewlett-Packard, USA) were used to observe the emission properties of the GQDs. For the
55 high-resolution micro-photoluminescence analysis, GQD suspensions were prepared directly
56 in quartz tubes after the dialysis process. Each AFM image of the GQDs was obtained by a
57 Nanoman (Veeco, Korea) instrument with premium high-resolution tapping-mode silicon
58 probes. The zeta potentials were measured using an ELS-Z2 instrument (Otsukael, Japan).
59 For the imaging of the luminescence of the GQDs, a 15 W Vilber Lourmat UV Lamp (VL-
60 215.M, France) was used as an excitation source (312 nm).



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62 **Figure S1 - Physicochemical characterization of GQDs purified by salting-out. High-**
 63 **resolution XPS narrow scans of the C1s region: The GQD50 (black), GQD100 (red),**
 64 **GQD300 (blue), and GQD500 (green). XPS analysis reveals the presence of C-C at 284.5**
 65 **eV (GQD50: 53.91 %, GQD100: 74.19%, GQD300: 73.48 %, GQD500: 73 %), C-O at**
 66 **286 eV (GQD50: 32.24 %, GQD100: 17.67 %, GQD300: 18.25 %, GQD500: 17.59 %),**
 67 **C=O at 287.5 eV (GQD50: 8.88 %, GQD100: 4.62 %, GQD300: 4.64 %, GQD500: 4.85**

68 %) and O-C=OH at 288.5 eV (GQD50: 4.97 %, GQD100: 3.51 %, GQD300: 3.64 %,
69 GQD500: 4.56 %)

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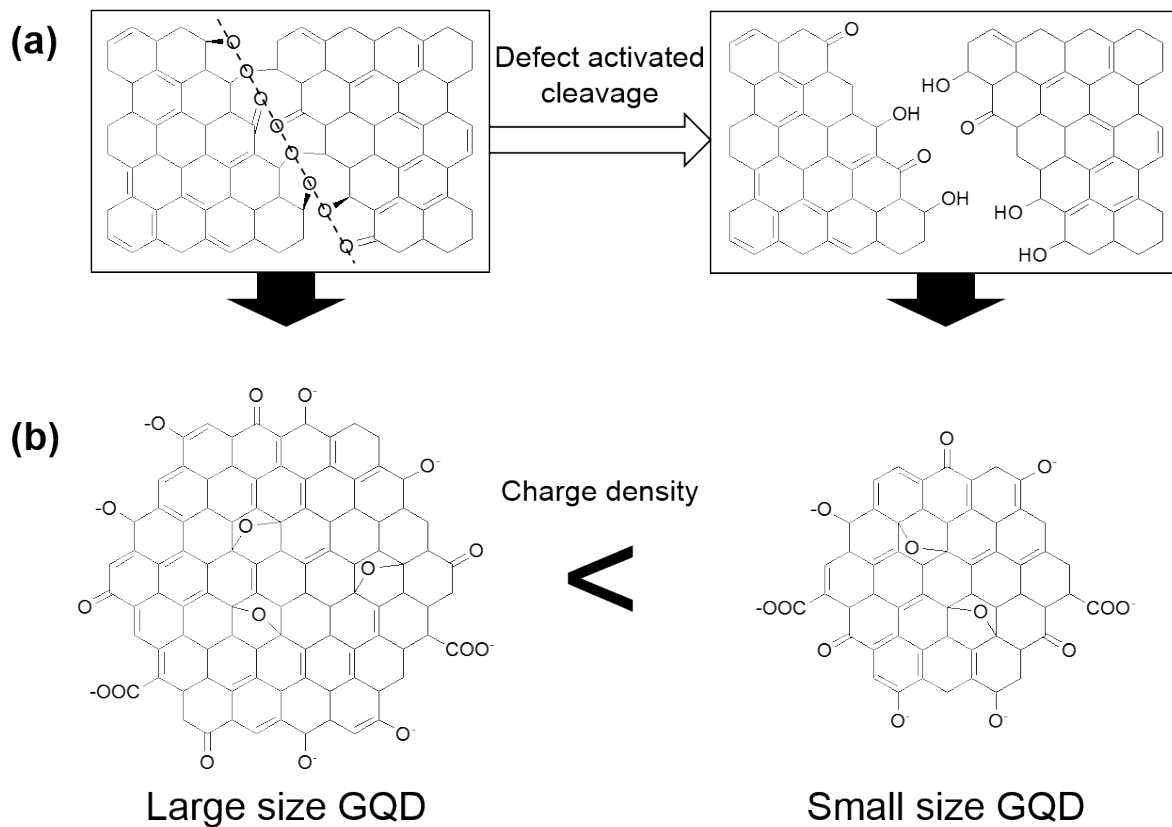
71 The high-resolution C1s spectra showed the differences in the carbon chemistries
72 between the GQD50 and GQD100 samples. The major C-C photoelectron peak which
73 appeared at 284.5 eV was more significant in GQD100 (second, red) than that in GQD50
74 (first, black). The area under the C-C curve was 53.9 % for GQD50, and this increased to
75 74.2 % for GQD100. The increased C-C photoelectron was unchanged for GQDs
76 purified with higher concentrations of ammonium sulfate (blue for GQD300 and green
77 for GQD500). In general, large GO or GQD (> 20 nm) samples are associated with
78 higher oxidative levels than nano-sized GQDs smaller than 4 nm. In particular, the
79 oxidation of GQDs primarily appears at the edges with functional carboxyl or hydroxyl
80 groups. The reason for the edge distribution of the functional groups may be the
81 preferential chemical cleavage toward an on-plane oxygen-containing functional group
82 such as the epoxide and hydroxyl group [1, 2]. Thus, charges in GQDs occur mainly
83 along the periphery such that the charge density, which can be a determining factor as
84 regards the solubility, may increase when the size of the purified GQDs decreases.

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86 **References**

87 [1] D. Pan, J. Zhang, Z. Li and M. Wu, Adv. Mater., 2010, 22, 734.

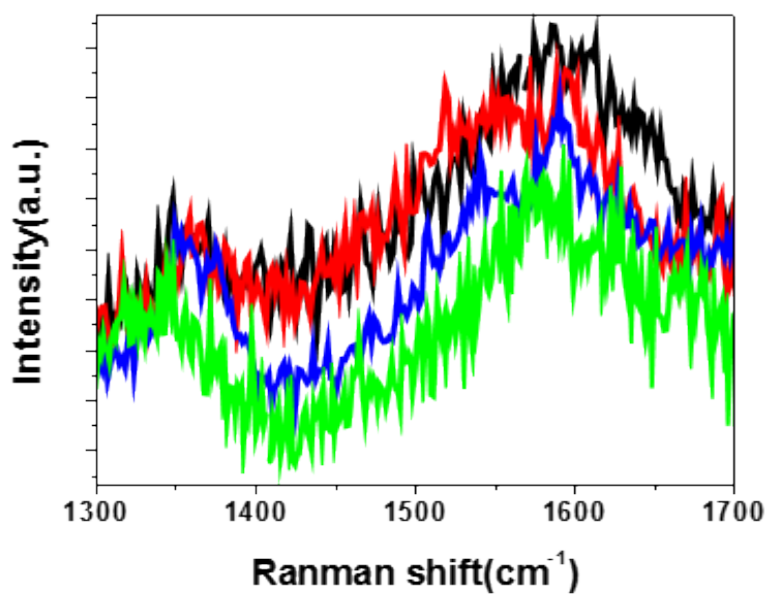
88 [2] J.-L. Li, K. N. Kudin, M. J. McAllister, R. K. Prud'homme, I. A. Aksay and R. Car, Phys.
89 Rev. Lett., 2006, 96, 176101.



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91 **Figure S2 - (a) Expected mechanism of defect activated cleavage of dissolved GQDs. (b)**

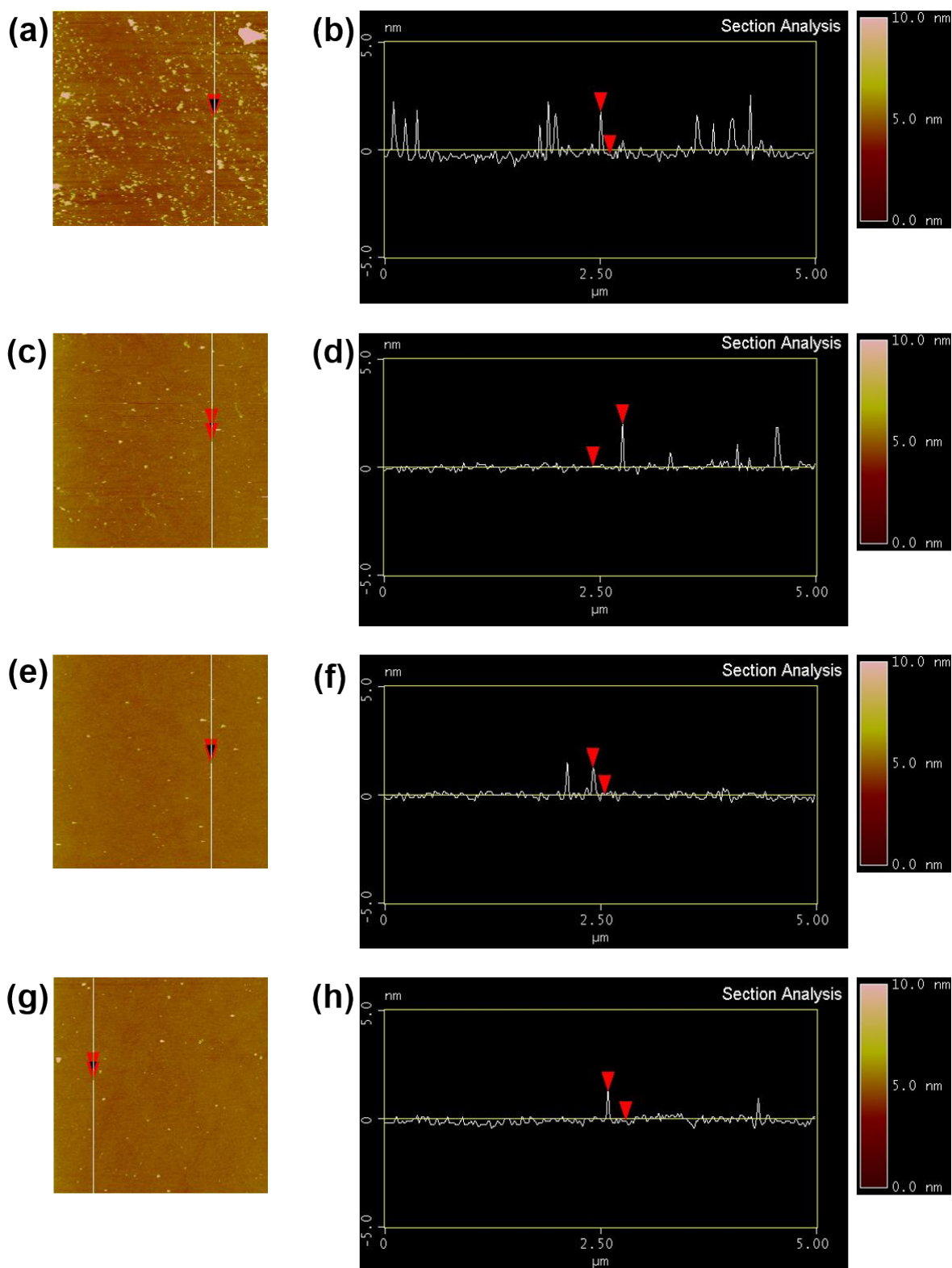
92 **Relationship between size and charge density of GQDs.**



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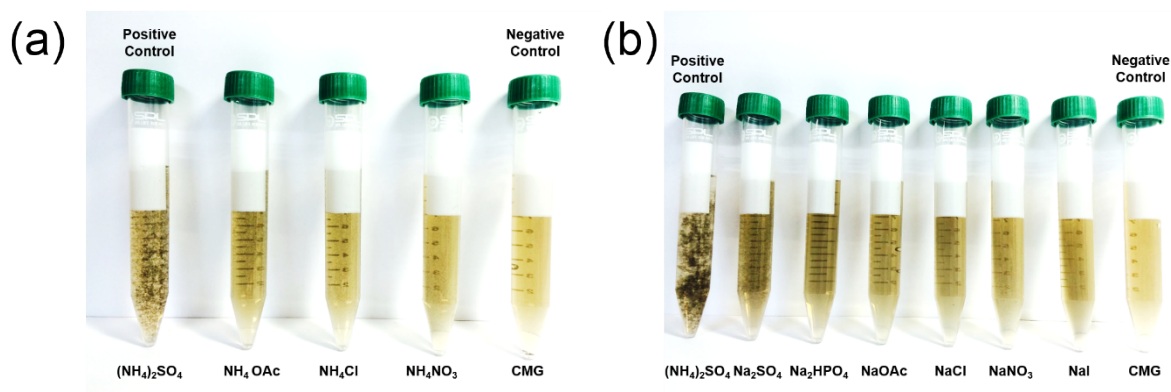
94 **Figure S3 - Raman spectra of the D and G bands of GQD50 (black), GQD100 (red)**

95 **GQD300 (blue), and GQD500 (green)**



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97 **Figure S4 - AFM images and height profiles of GQDs. Typical corresponding**
 98 **distributions of (a) GQD50; (b) its line scan image; (c) GQD100; (d) its line scan image;**
 99 **(e) GQD300; (f) its line scan image; (g) GQD500; (h) its line scan image**



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101 **Figure S5 - Salting-out effect of various salts regarding CMG suspension. A low**
 102 **soluble fraction of CMGs was salted-out by series of ammonium containing salts**
 103 **(a) and sodium containing salts (b). All salt concentration was fixed to 50 mM.**

104 CMG was prepared by a modified Hummer's method. To produce the CMG
 105 suspension, the prepared GO powder was dispersed in DI water with concentration of
 106 0.1mg/ml by way of ultrasonication for 30 minutes. Various kinds of salts were added
 107 into each GO solution with 50 mM salt concentration.