Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Raman spectroscopy of bottom-up synthesized graphene quantum dots: size and structure dependence

Enkeleda Dervishi,[†] Zhiqiang Ji,[‡] Han Htoon, [†] Milan Sykora,[‡,§] and Stephen K. Doorn[†*]

[†]Materials Physics and Applications Division, Center for Integrated Nanotechnologies, [‡]Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

[§]Present address: Laboratory for Advanced Materials, Faculty of Natural Sciences, Comenius University, 84215 Bratislava, Slovakia

Table S1: Graphene quantum dots (GQDs) with 19, 48 and 79 ordered carbon rings and their corresponding dimensions.

Sample Name	**Number of sp^2 Carbons (n)**	**Number of Conjugated Rings (N_{CR})**	**Size (L in nm)**
GQD(1)	60	19	0.97
GQD(2)	132	48	1.51
GQD(3)	204	79	1.62

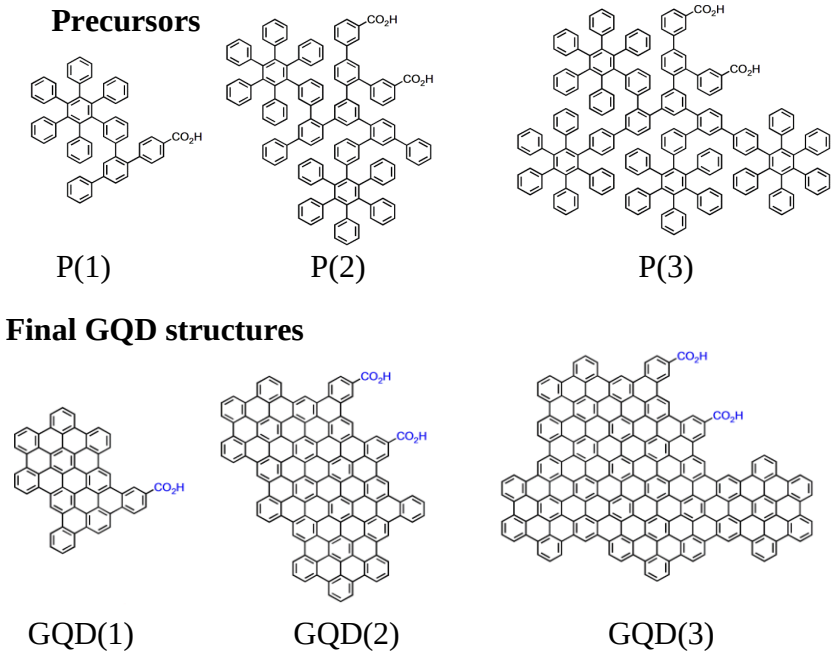

Fig. S1: Chemical structures of the precursors (P(i)) and the corresponding graphene quantum dots (GQD(i)).

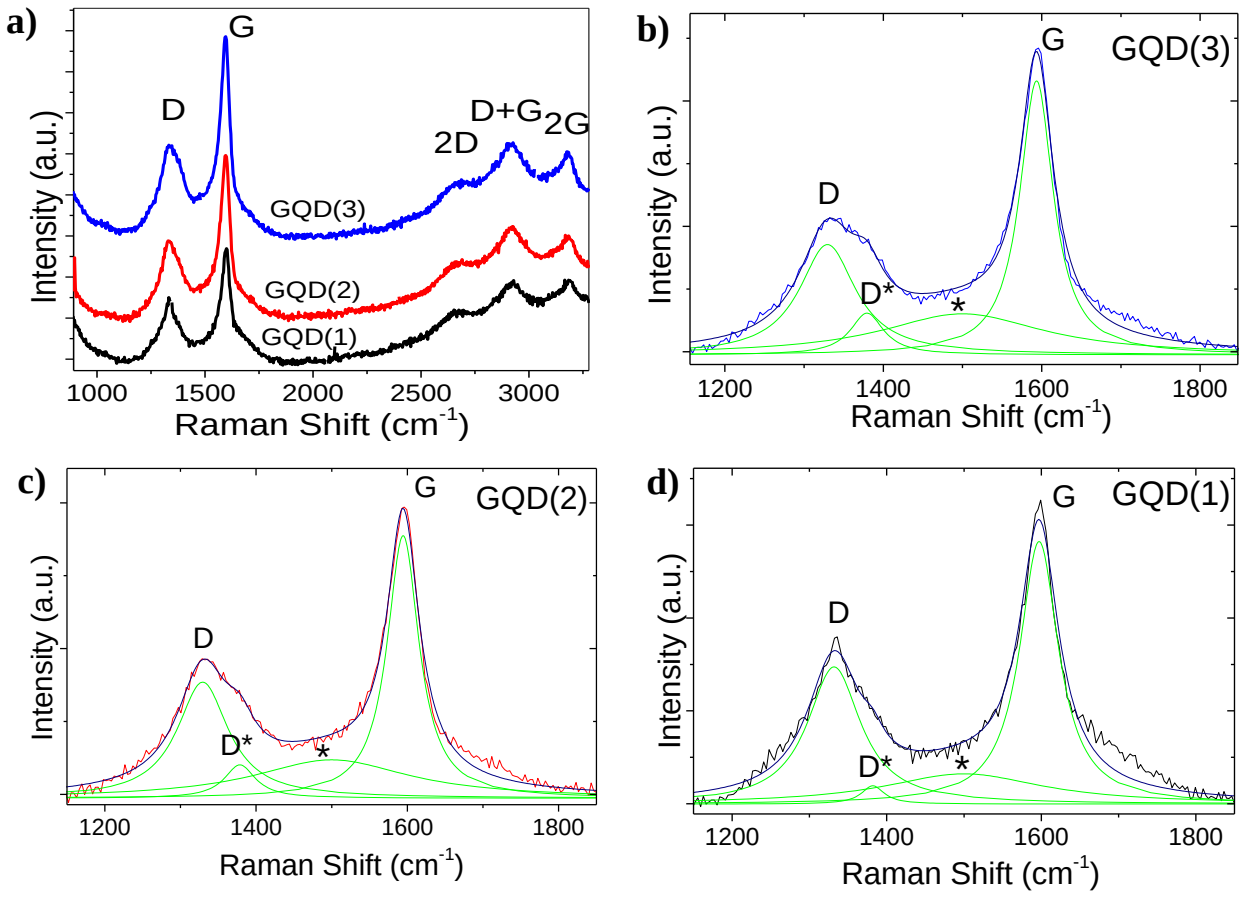

Fig. S2. (a) Raman spectra of graphene quantum dots with various sizes recorded with 405 nm excitation wavelength. (Spectra are vertically offset for clarity). (b-d) Zoom of D and G band spectral region and deconvolution of D and G bands using Lorentzian fits.

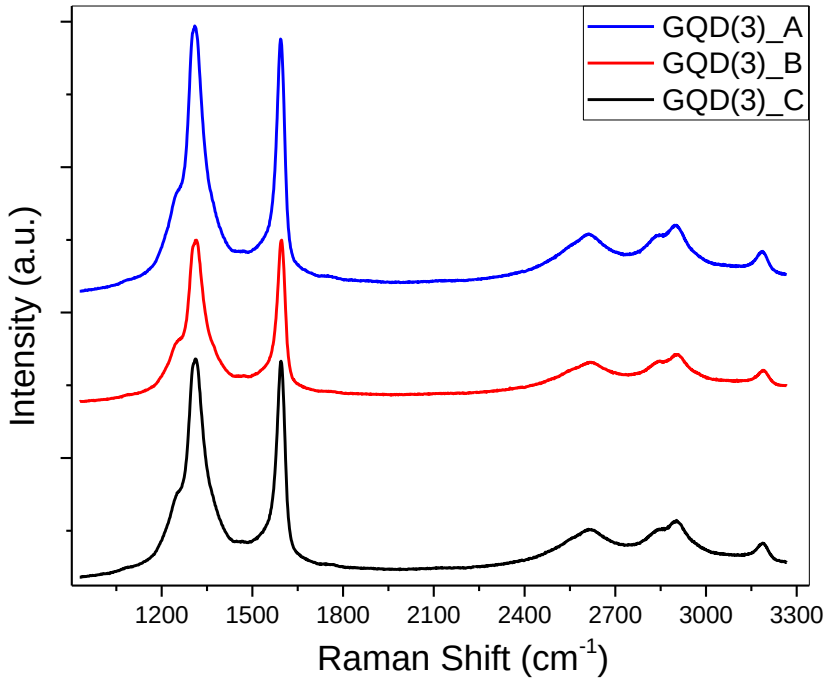

Fig. S3: Raman spectra (532 nm exc.) of GQD(3) taken at 3 separate locations on the same film. Similarity in appearance indicates a high degree of homogeneity in the GQD synthesis.

Model Relating I_D/I_G to L_D for Disordered Large-Area Graphene and Relation to Data for GQDs:

As noted in the main text, the D-to-G-band intensity ratio in intentionally disordered large-area graphene has been described by Jorio et al.[1,2] as the sum of contributions from the activated area in the region within the Raman coherence length of the defects and from the disordered region itself:

$$\frac{I_D}{I_G} = C_A f_A + C_S f_S \quad \text{(S1)}$$

In eq. 1, f_A is the fractional activated area, while f_S is the fractional disordered area of the defects themselves, with C_A and C_S being the respective scaling coefficients. The expression may be expanded in terms of the radius of the activated and disordered regions (r_A and r_S, respectively) and the inter-defect distance L_D:[1]

$$\frac{I_D}{I_G} = C_A \frac{(r_A^2 - r_S^2)}{(r_A^2 - 2r_S^2)} \left[e^{-\frac{\pi r_S^2}{L_D}} - e^{-\pi(r_A^2 - r_S^2)/L_D}\right] + C_S \left[1 - e^{-\frac{\pi r_S^2}{L_D}}\right] \quad \text{(S2)}$$

In the case for which both the activated and disorder terms are included in the determination, C_A is taken as 4.2, and C_S is taken as 0.87.[1] In the absence of the disorder term (*i.e.* $C_S = 0$), C_A is taken as 4.72.[2] r_A in both cases is taken as 3 nm and r_S as 1 nm. These values were obtained for laser excitation at 514 nm, while our data was obtained with excitation at 532 nm. It has been shown that the I_D/I_G ratio is proportional to the inverse fourth power of the excitation energy (E).[2] To correct for the different excitation energy, the model results calculated from eq. S2 (shown in Fig. 4b of the main text) were multiplied by $(532/514)^4$.

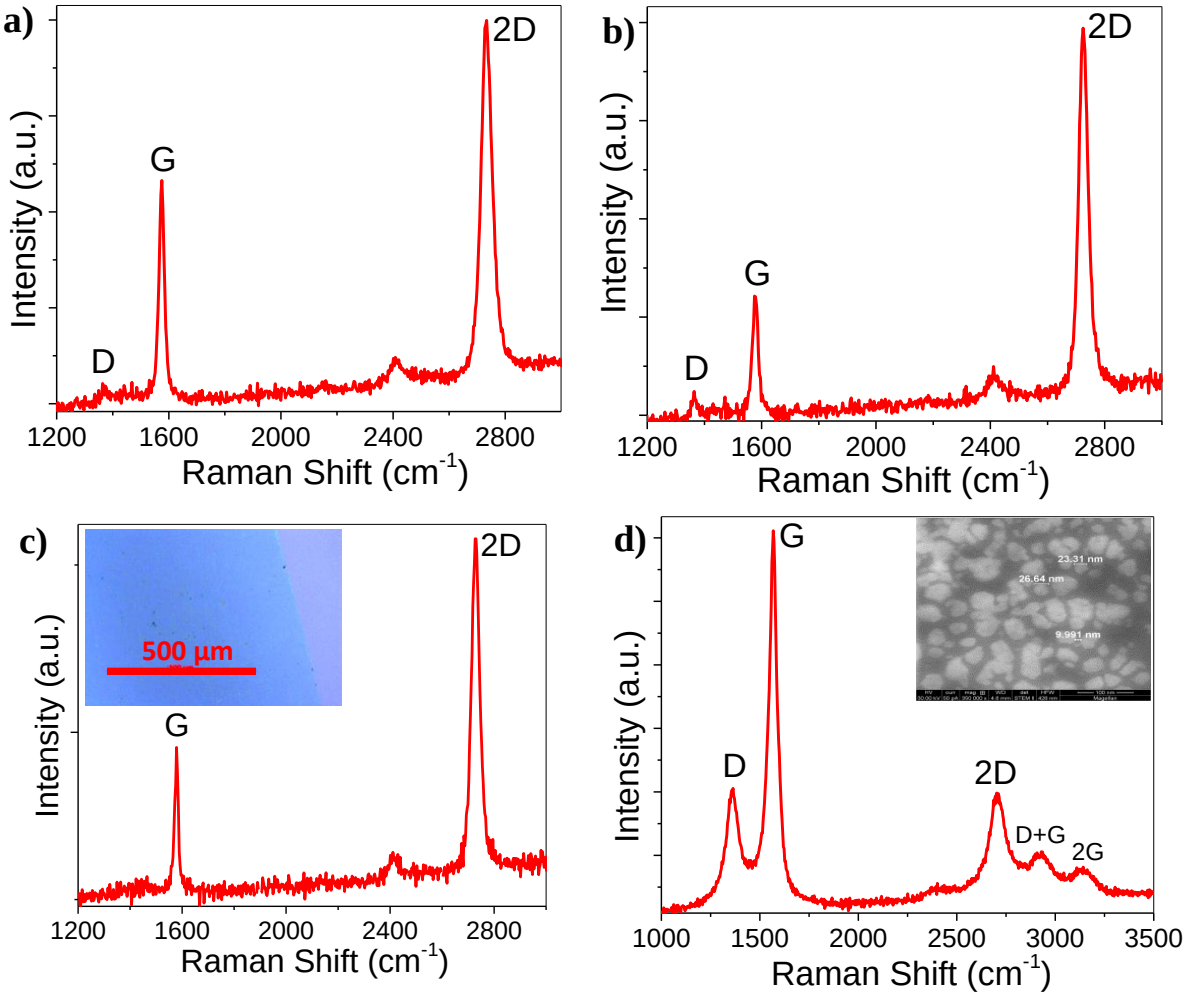

Fig. S4: (a-c) Raman spectra of large area graphene recorded with 405 nm excitation at three different positions. The inset shows an optical microscopy image of large-area graphene transferred over Si/SiO_2 wafer (scale bar: 500 µm). (d) Raman spectrum of nano-graphene platelet structures recorded with 405 nm excitation. The inset shows an SEM image of typical platelet structures and their size distribution.

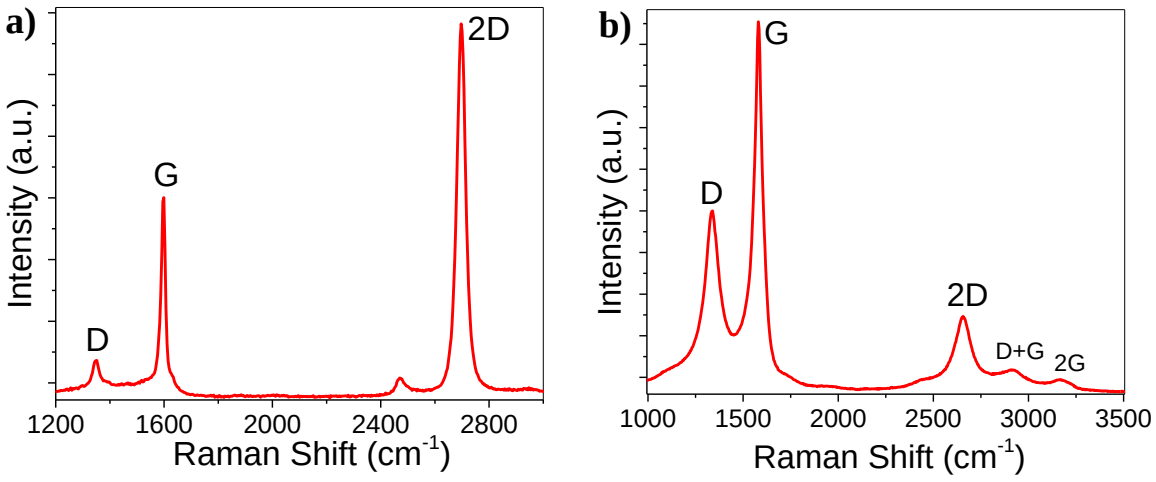

Fig. S5: Raman recorded with 532 nm excitation for (a) large area graphene and (b) nano-graphene platelets.

The intensity of the 2D band in the Raman spectrum of a single-layer large-area graphene with very few defects becomes larger than that of the G band, while the rest of the second order bands disappear.[3] The average D and G frequencies for nano-graphene platelets recorded with 405 nm excitation were found to be 1360 cm^{-1} and 1567 cm^{-1}, respectively. The average D and G frequencies for large-area graphene recorded with 405 nm excitation were found to be 1367 cm^{-1} and 1576 cm^{-1}, respectively. The average D and G frequencies for nano-graphene platelets recorded with 532 nm excitation were found to be 1337 cm^{-1} and 1587 cm^{-1}, respectively. The average D and G frequencies for large-area graphene recorded with 532 nm excitation were found to be 1351 cm^{-1} and 1594 cm^{-1}, respectively.

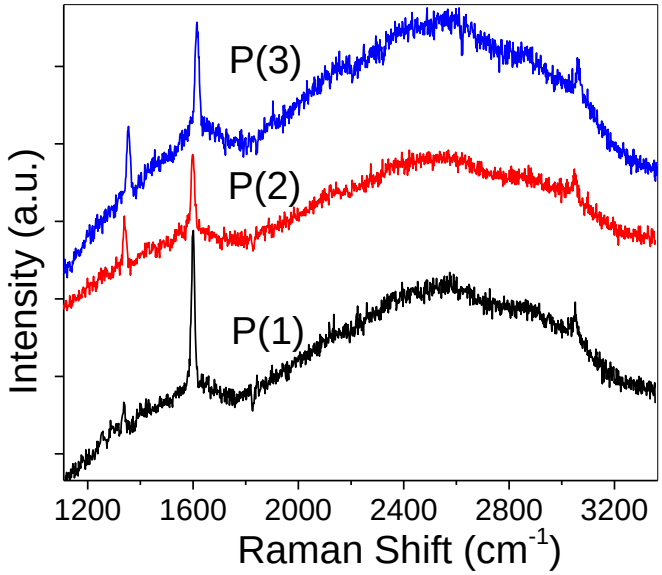

Figure S6: Raman spectra of the precursors used to synthesize the graphene quantum dots, recorded with 532 nm excitation. (Spectra are vertically offset for clarity).

References

1. M. M. Lucchese, F. Stavale, E. H. Martins Ferreira, C. Vilani, M. V. O. Moutinho, R. B. Capaz, C. A. Achete and A. Jorio, *Carbon*, 2010, 48, 1592-1597.

2. L. G. Cancado, A. Jorio, E. H. Martins Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala and A. C. Ferrari, *Nano Lett.*, 2011, 11, 3190-3196.

3. E. H. M. Ferreira, M. V. O. Moutinho, F. Stavale, M. M. Lucchese, R. B. Capaz, C. A. Achete and A. Jorio, *Phys. Rev. B*, 2010, 82, 125429.