Electronic Supplementary Material (ESI) for Chemical Communications

Facile synthesis of graphitic carbon quantum dots with size tunability and uniformity using reverse micelles

Woosung Kwon and Shi-Woo Rhee*

System on a Chip Chemical Process Research Center,

Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, South Korea;

E-mail: srhee@postech.ac.kr ; Tel: +82-54-279-2265; Fax: 82-54-279-8619

*Corresponding author. E-mail: srhee@postech.ac.kr

Tel: 82-54-279-2265; Fax: 82-54-279-8619

Electronic Supplementary Information (ESI)

Experimental details

All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise specified. Bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT) was dried at 90 °C under argon flow for 3 h prior to use. A solution of AOT (880 mg, 0.1 mol) in decane (20 mL) was prepared and degassed in the reaction flask under argon flow for 1 h. An aqueous solution of glucose (10 wt%) was then injected into the reaction flask under vigorous stirring at various *w* ratios of 10 (0.36 mL, 1 mol), 20 (0.72 mL, 2 mol), 30 (1.08 mL, 3 mol), and 40 (1.44 mL, 4 mol). The turbid resulting solution became transparent in a few seconds to indicate the formation of reverse micelles (water-in-oil phase). Subsequently, the reaction flask was flushed by argon and the micellar solution was aged for 12 h at room temperature under vigorous stirring. Hexadecylamine (HDA, 1.44 g, 0.3 mol, excess) was then added to the solution. The mixture was immediately refluxed at 160 °C under argon flow for 5 h. After cooling down to room temperature, the product was centrifuged at 3,000 rpm for 30 min and the flocculate was discarded. The brown-colored supernatant was then heated at 200 °C under argon flow to remove the residual solvent. The resulting colloidal GQDs were washed with hexane three times and finally re-dispersed in octane.

For the spectroscopic measurements, the colloidal GQDs were dispersed in anhydrous toluene. Fourier transform infrared (FT-IR) spectroscopy was performed using a spectrometer (Nicolet 6700, Thermo) Absorbance spectra were recorded using a spectrophotometer (Optizen POP, Mecasys). Photoluminescence spectra were measured using a fluorometer (FP-6500, Jasco). Transmission electron microscope (TEM) images were obtained using Jeol JEM-2200FS with the image Cs-corrector at an accelerating voltage of 200 kV. Quantum yield measurements were referred to Lakowicz, J. R. “Principles of Fluorescence Spectroscopy”, 2nd Ed., 1999, Kluwer Academic/Plenum Publishers, New York. A quinine

sulphate solution in 0.1 M H_2SO_4 (the literature quantum yield of 54 % at 360 nm) was used as a standard. The purified GQDs were dissolved in toluene at the same concentration of 5 mg ml^{-1}. The calculation of quantum yields were accompanied with the following equation:

$$Q = Q_S \left(\frac{I}{I_S}\right)\left(\frac{F_S}{F}\right)\left(\frac{n}{n_S}\right)^2$$

where Q is the quantum yield, I is the integrated area under the emission spectrum, F is the absorbance (optical density, D) at the excitation wavelength ($F = 1 - 10^{-D}$), and n is the refractive index of the solvent. In all cases, the subscript "S" stands for the standard. For all measurements, the 10 mm cuvettes were pre-stored under the excitation wavelength in order to minimize re-absorption.

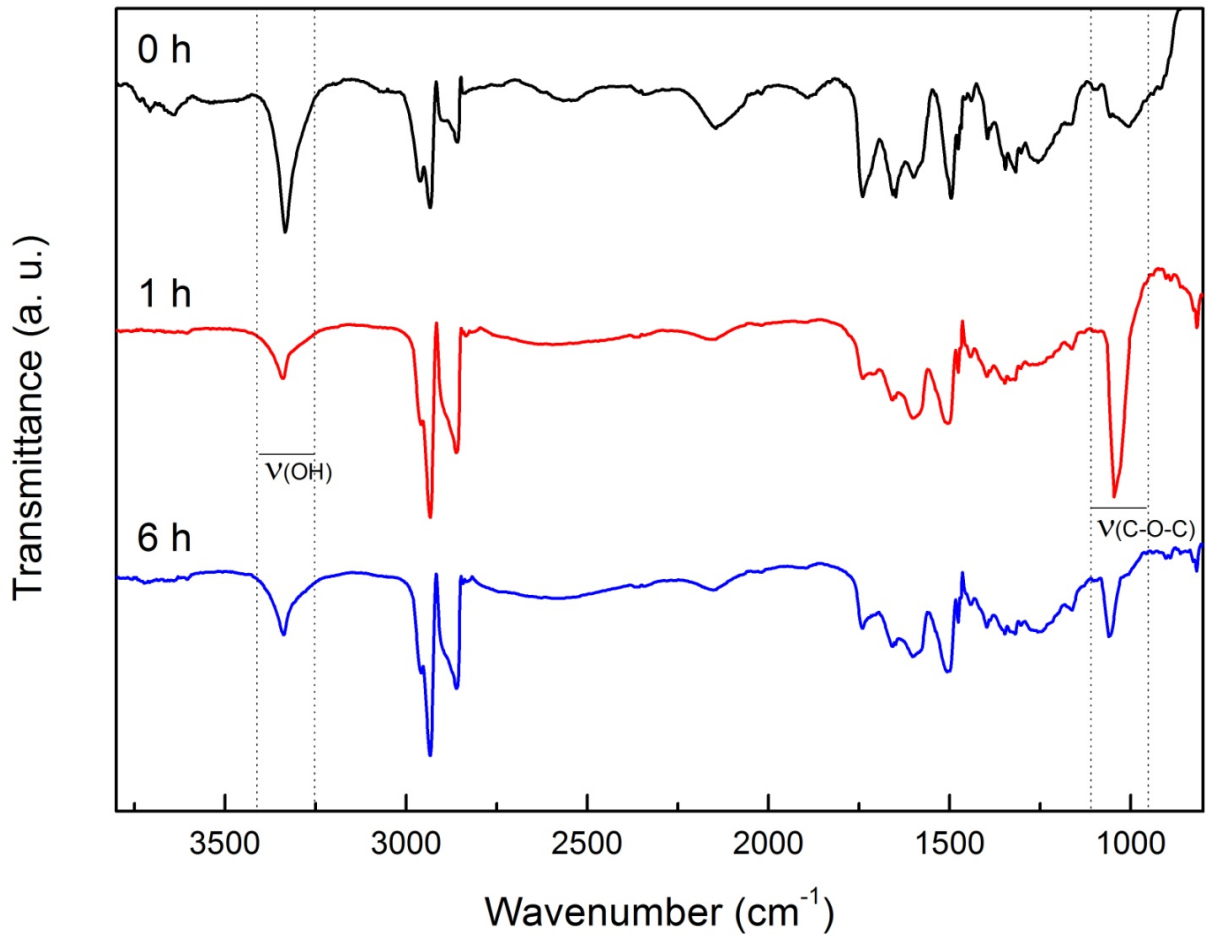

Fig. S1 After 1 h, the color of the solution turns to orange and the symmetric vibrations of C-O-C (near 1200 cm^{-1}) become prominent due to the formation of oligosaccharides. This peak degrades with the progress of the reaction because of the formation of sp^2 carbon cores spurred by the pyrolytic carbonization. Also, the vibrations of OH (near 3300 cm^{-1}) diminishes during the reaction due to the decomposition of C-OH bonds.

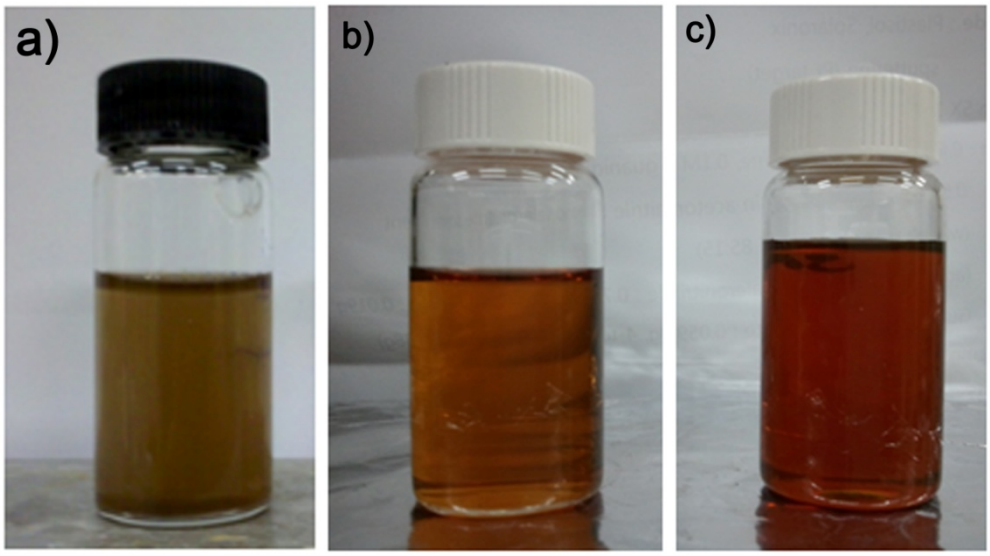

Fig. S2 A role of AOT at high temperature to prohibit aggregation between reactants. Pictures of products synthesized in different conditions: (a) without AOT, (b) with AOT (bare GQDs), and (c) with AOT further passivated by HDA (HDA-capped GQDs). The product in (a) is opaque and contains bulk aggregates precipitated at the bottom of the vessel whereas the others are clear and homogeneous.

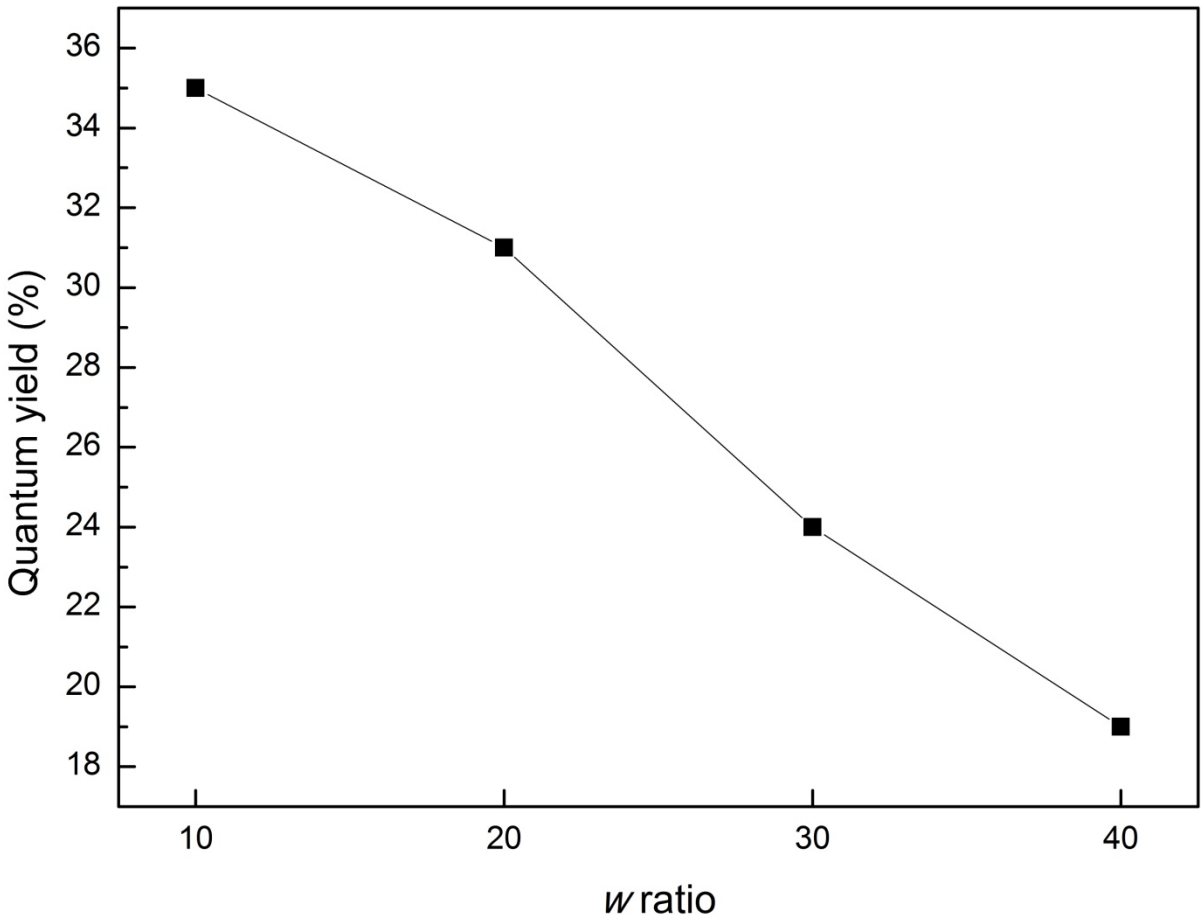

Fig. S3 Quantum yields of HDA-capped GQDs at various *w* ratios.

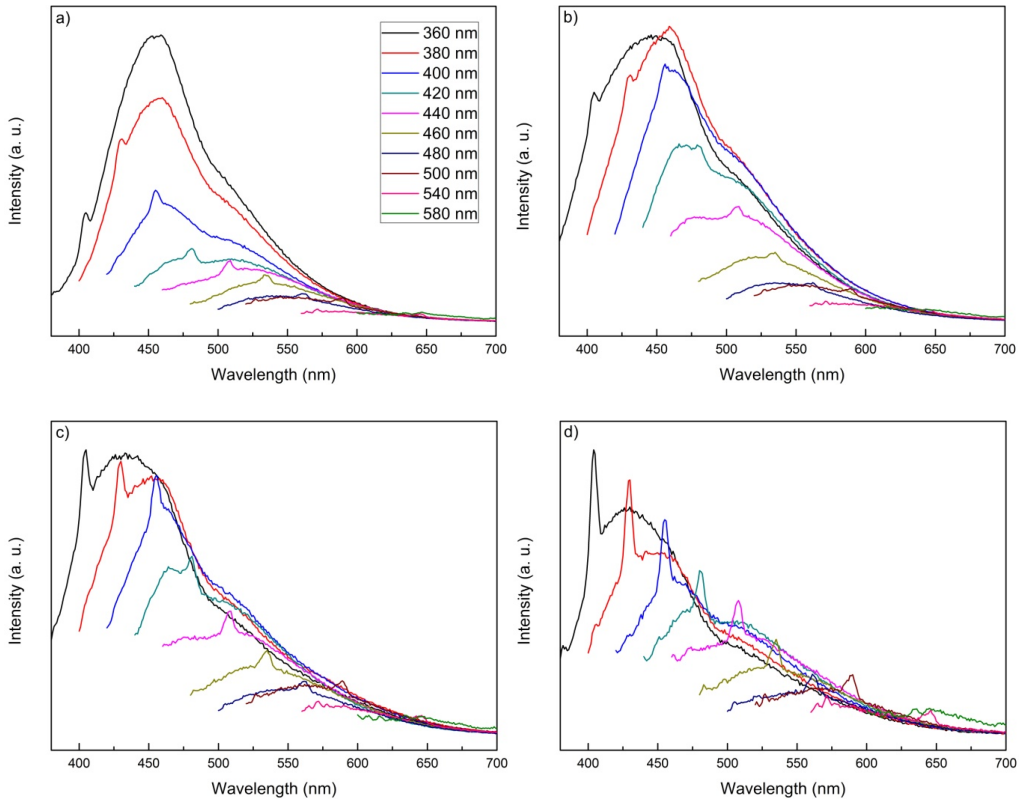

Fig. S4 Photoluminescence spectra of bare GQDs at various *w* ratios: (a) 10, (b) 20, (c) 30, and (d) 40, and their corresponding quantum yields. Because the surface inhomogeneity of bare GQDs is inferior to that of HDA-capped GQDs, the photoluminescence intensity is relatively poor. Because of the low intensity, specific photoluminescence peaks (not shown in Fig. 3) are relatively developed. Such peaks become prominent as the size of the GQDs increases due to the decrease of the surface-to-volume ratio. For the origin of the additional peak, we may propose two possibilities:

(a) Effects of unreacted precursors: unreacted glucose molecules can be bound on the surface as a form of oligosaccharides, which may induce a certain degree of surface inhomogeneity and impart the one another peak.

(b) Effects of surfactants bounded on the surface: the surfactant (AOT) can be tightly bounded on the surface and thus may give additional surface inhomogeneity. Its characteristic would be different from carbon so that can introduce the abnormal peak.

According to one of our former experiments, after post-passivation of the bare dots using HDA (excluded in the paper), the PL spectra were recovered to the almost same level as those in Fig. 3 and finally there remains only one peak. This result may help to prove the proposed interpretation.

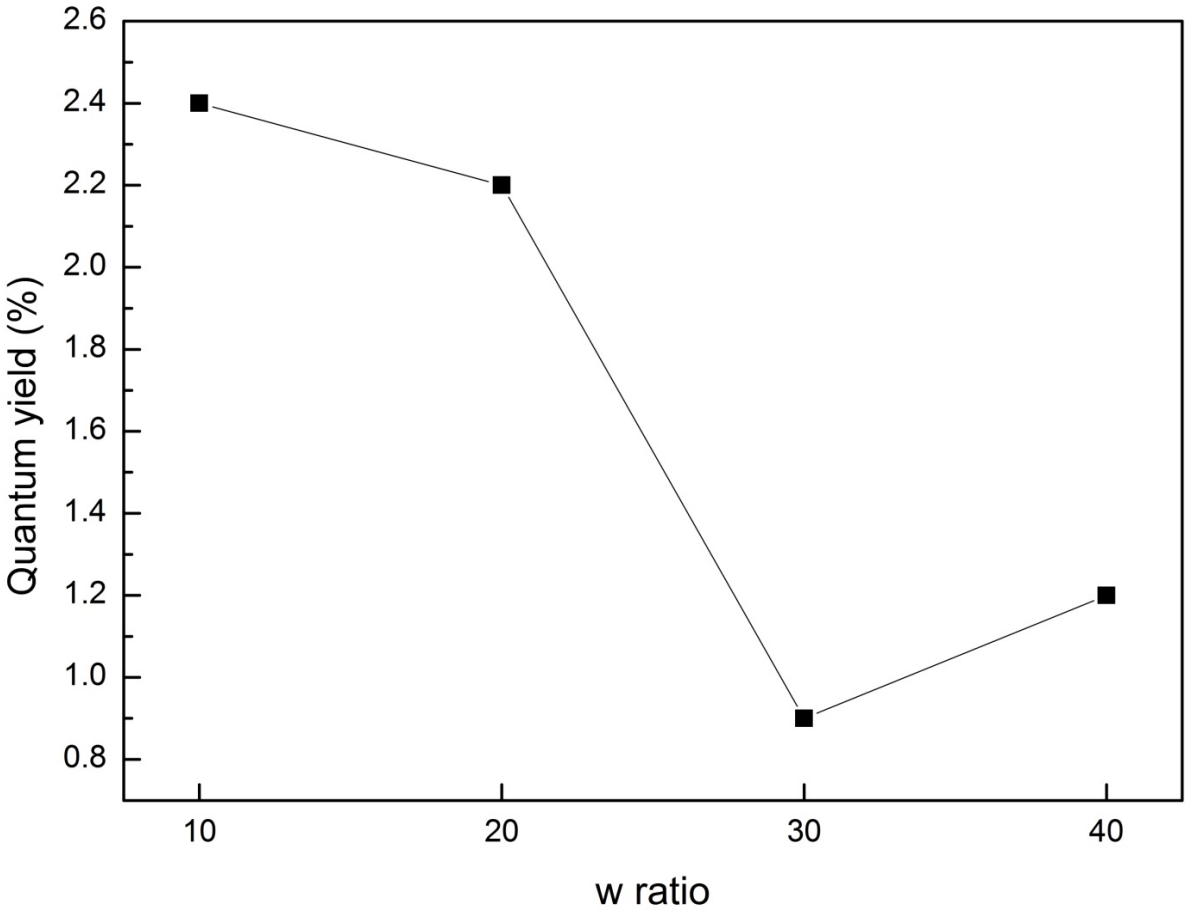

Fig. S5 Quantum yields of bare GQDs at various *w* ratios. Because the surface inhomogeneity of bare GQDs is inferior to that of HDA-capped GQDs, the quantum yields are relatively poor.

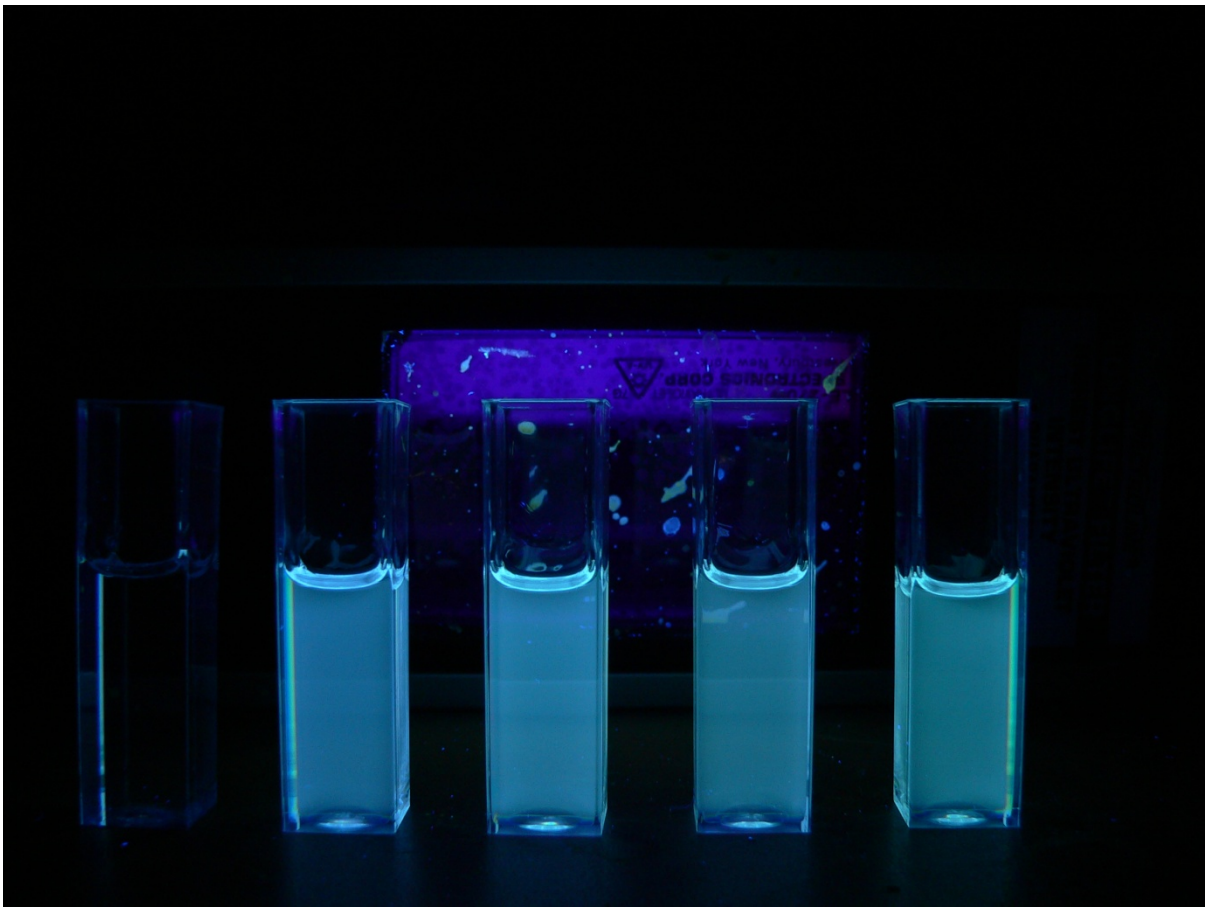

Fig. S6 Several samples of GQDs in toluene under UV illumination. The leftmost one is toluene for comparison.