Supplementary Data

Biomimetic Colloidal Photonic Crystals by Coassembly of Polystyrene Nanoparticles and Graphene Quantum Dots

Dali Huang [a,1], Minxiang Zeng [b,1], Ling Wang [b,1], Lecheng Zhang [b], Zhengdong Cheng [a, b*]

[a] Department of Materials Science & Engineering, Texas A&M University, College Station, Texas, 77843, United States

[b] Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas, 77843, United States

Content

1. Abbreviations in this supplementary data

* Corresponding author.

E-mail address: zcheng@tamu.edu (Z. Cheng)

Tel. number: 979.845.3413

[1] These authors contributed equally to this work.

PS: Polystyrene.

PCs: Photonic crystals.

GQDs: Graphene Quantum Dots.

GQDs-x : The synthesized graphene quantum dots which reacted for x hours, x was the hydrothermal reaction time. (For example, 3 hours, 5 hours, and 7 hours of hydrothermal pyrolysis of GQDs would be referred to as GQDs-3, GQDs-5 and GQDs-7, respectively.)

PS/GQDs: PS photonic crystals with GQDs.

PS/GQDs-x : the PS photonic crystals with GQDs which underwent x hours hydrothermal reaction. (For example, 3 hours, 5 hours, and 7 hours of hydrothermal pyrolysis of GQDs with PS photonic crystals would be referred to as PS/GQDs-3, PS/GQDs-5 and PS/GQDs-7, respectively.)

2. Morphology and characterization of graphene quantum dots (GQDs)

2.1. Atomic Force Microscopy (AFM) image of GQDs

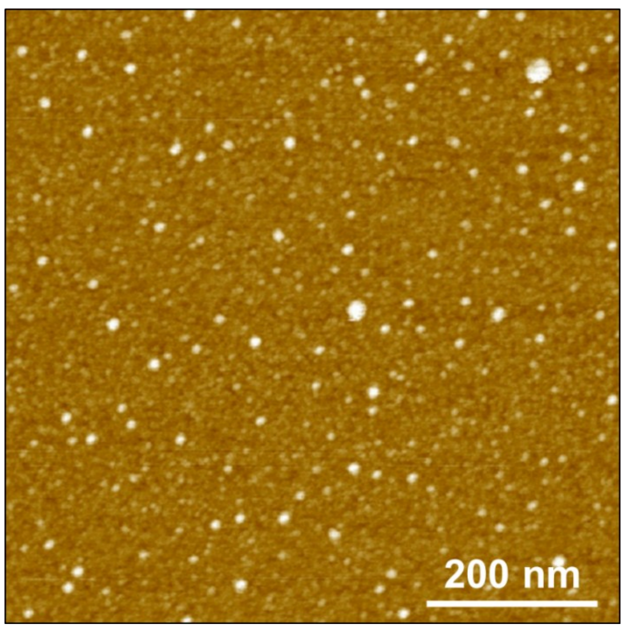

Fig. S1. AFM image of graphene quantum dots (7 hours of hydrothermal reaction).

The physical morphology of GQDs which synthesized of 7 hydrothermal hours at 200 °C oven was studied through Bruker Dimension Icon AFM, as shown in **Fig. S1**. The average size of GQDs was 12.1 nm.

2.2. Transmission Electron Microscope (TEM) image of GQDs

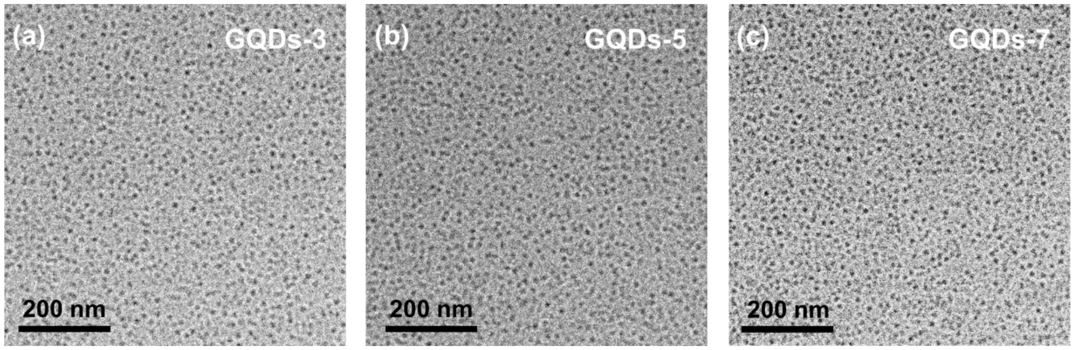

Fig. S2. TEM image of GQDs of various hydrothermal time (3hr, 5hr, 7hr).

The average size of GQDs-3, GQDs-5, GQDs-7 achieved from TEM was 12.3 nm, 12.8 nm and 12.0 nm, all GQDs were narrowly size distributed.

2.3. X-ray photoelectron spectroscopy (XPS) of GQDs

Table S1. XPS chemical state of GQDs of different reaction time

Bonding States	C-C (counts)	C=O (counts)	C-C/C=O (calculated ratio)
GQDs-3	16681.57	8135.6	2.05
GQDs-5	16127.45	6960.3	2.32
GQDs-7	17343.21	5874.6	2.95

In **Table S1**, the peak intensities of C-C and C=O of GQDs were acquired from **Fig. 2b** and C-C/C=O ratios were calculated. The binding energy of C-C was 284.8 eV and of which C=O was 288.6 eV.

3. Normalized reflectance peak intensity of enhanced PS/GQDs photonic

crystals

3.1. GQDs hydrothermal reaction time variance (3 hours, 5 hours, 7 hours)

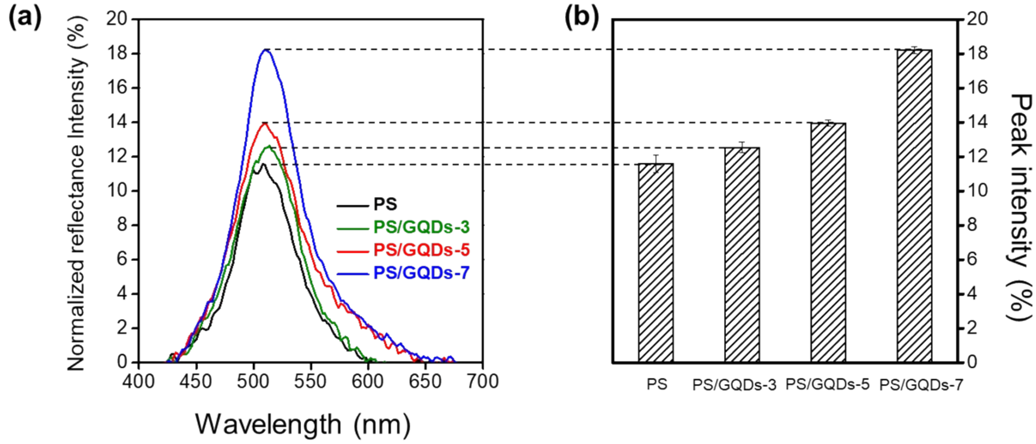

Fig. S3. (a) Normalized reflectance intensity of the PS/GQDs photonic crystals with various GQDs fabrication reaction time (3 hours, 5hours, 7 hours). (b) Corresponding reflectance peak intensity of the PS/GQDs photonic crystals. (The size of PS nanoparticles was 214 nm. GQDs-3, GQDs-5 and GQDs-7 were at the same 1 wt% concentration).

Fig. S3a exhibited the normalized reflectance intensity of PS/GQDs corresponding to the data from **Fig. 3c**. There was no clear peak wavelength shift at various GQDs fabrication reaction time in **Fig. S3a**. And **Fig. S3b** showed the bar chart of corresponding PS/GQDs enhanced photonic crystals intensity.

3.2. GQDs concentration variance (0 wt%, 0.1 wt%, 0.5 wt%, 1wt%)

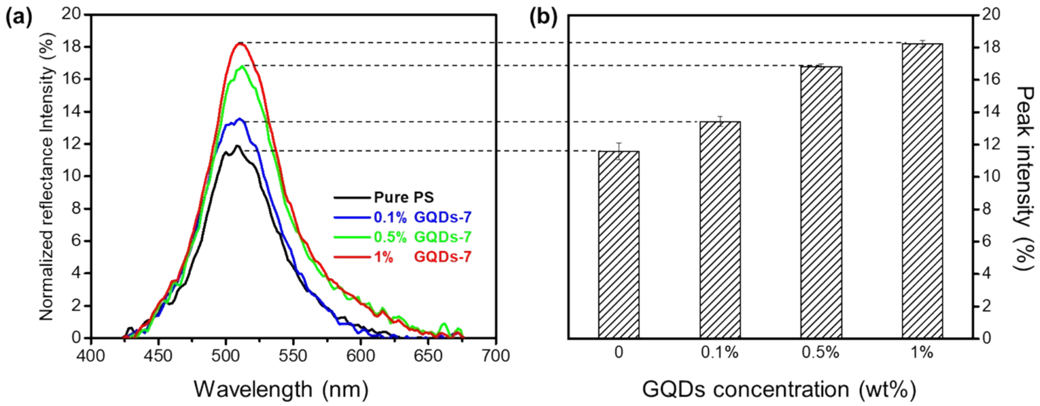

Fig. S4. (a) Normalized reflectance intensity of the PS/GQDs photonic crystals with various GQDs concentration (0 wt%, 0.1 wt%, 0.5 wt% and 1 wt%). (b) Corresponding reflection peak intensity of PS/GQDs photonic crystal films. (The size of PS nanoparticles was 214 nm. GQDs underwent hydrothermal reaction for 7 hours.)

Fig. S4a represented the normalized reflectance intensity of PS/GQDs corresponding to the data from **Fig. 4**. And **Fig. S4b** exhibited the bar chart of PS/GQDs-7 reflectance intensity with different GQDs concentration (0 wt%, 0.1 wt%, 0.5 wt%, 1wt%).

4. Scanning electron microscopy image (SEM) of polystyrene nanoparticles

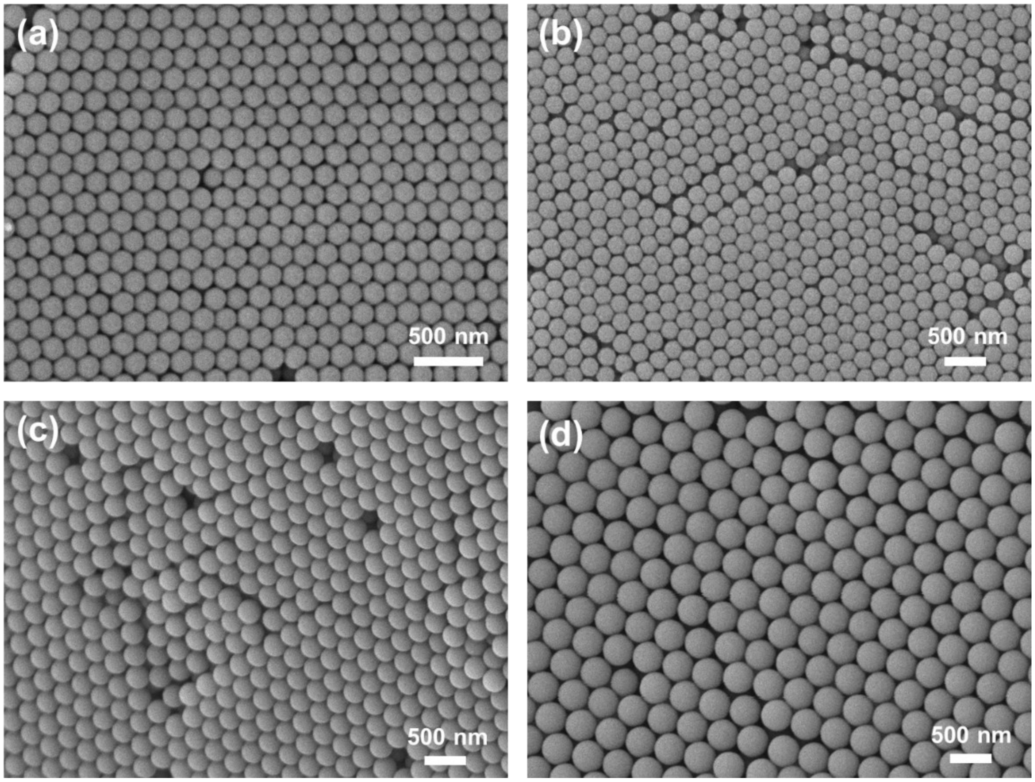

Fig. S5. SEM images of PS nanoparticles. The average size of each is: (a) 192 nm, (b) 214 nm, (c) 274 nm, (d) 396 nm.

Four kinds of PS nanoparticles were investigated through SEM images, as shown in **Fig. S5**. From the figures, all PS nanoparticles were uniform in sizes and formed ordered lattice structures. The average sizes of PS nanoparticles were averagely measured as 192 nm, 214 nm, 274 nm and 396 nm through ImageJ software analysis.

5. Dynamic light scattering size measurement of polystyrene nanoparticles

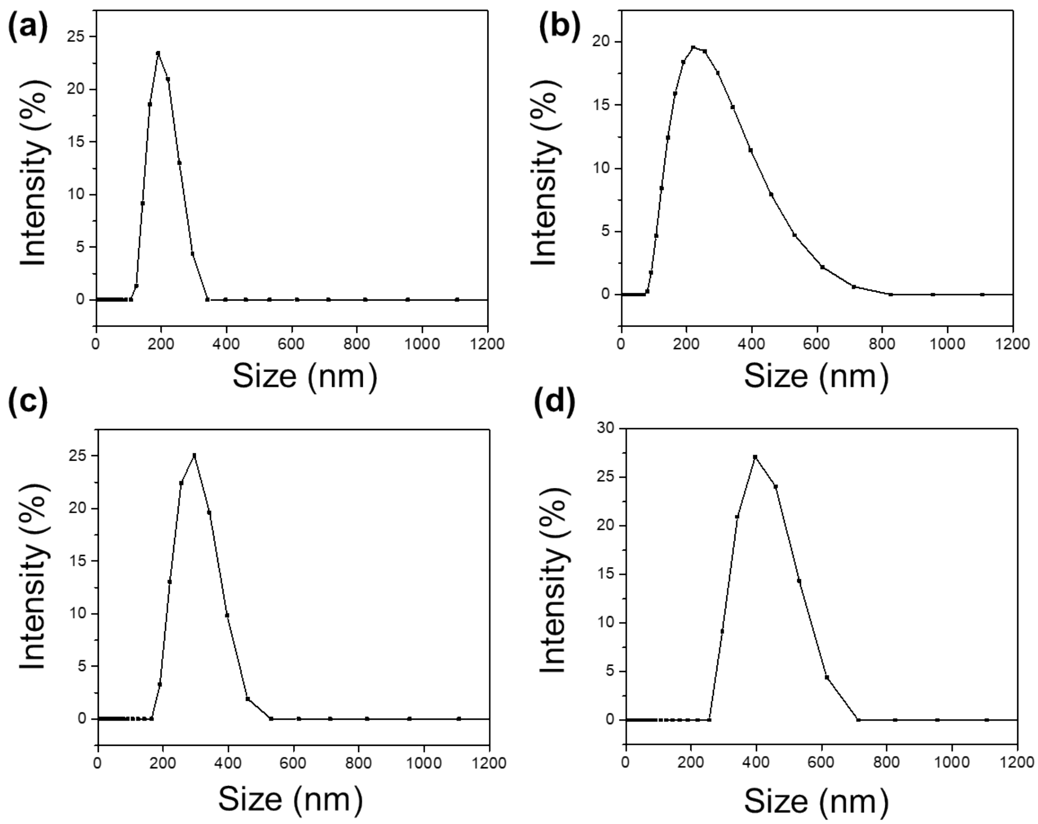

Fig. S6. DLS size measurement of PS nanoparticles. (a) 192 nm, (b) 214 nm, (c) 274 nm, (d) 396 nm.

Four kinds of PS nanoparticles were also studied through dynamic light scattering (DLS) size measurements, as shown in **Fig. S6**. The DLS data matched average size achieved from SEM.

6. Reflectance calculation of enhanced polystyrene photonic crystals through Bragg's Law.

Table S2. Reflectance peak calculation of PS/GQDs photonic crystals by Bragg's Law

PS/GQDs enhanced photonic crystals				
λ calculation (nm)	**453.18**	**505.11**	**646.73**	**467.35**
Diameter of PS (nm)	192	214	274	396
Structural Color				
$n_{effective}$	1.4454	1.4454	1.4454	1.4454
θ	0	0	0	0
K	1	1	1	2
Reflectance peak (nm) UV-vis spectrofluorometer	**446.00**	**510.00**	**640.00**	**472.00**

The reflectance wavelength λ of PS/GQDs enhanced crystals was calculated by Bragg's Law, as shown in **Table S2**. The effective refractive index $n_{effective}$ and calculated reflectance λ could be achieved by **Equation 1** and **2** below.

$$\lambda = \frac{1}{K} * 2\sqrt{\frac{2}{3}} D_{c-c}\sqrt{n_{effective}^{2} - \sin^2\theta} \quad \textbf{(1)}$$

$$n_{effective} = \emptyset_{PS} * n_{PS} + \emptyset_{Air} * n_{Air} + \emptyset_{GQDs} * n_{GQDs} \quad \textbf{(2)}$$

λ is the reflectance wavelength of light, K is the order of reflection, $D_{c\text{-}c}$ is diameter of PS nanoparticles (equivalent as the distance between two nearest nanoparticles), and incident angle θ is 0. n_{PS}, n_{Air} and n_{GQDs} represent refractive index of PS (n= 1.59), air (n= 1) and GQDs (n= 1.88), respectively. $Ø_{PS}$, $Ø_{air}$ and $Ø_{GQDs}$ represent the volume fraction of PS (Ø= 74%), air (Ø= 25%) and GQDs (Ø= 1%). $n_{effective}$ is herein calculated as 1.4454 through **Equation 2**. The λ of PS/GQDs films (PS sizes: 192, 214, 274, and 396 nm) were calculated through **Equation 1**. λ_{192}= 453.18 nm, λ_{214}= 505.11 nm, λ_{274}= 646.73 nm, λ_{396}= 467.35 nm, as shown in the first row in **Table S2**. And the last row of **Table S2** is the λ tested through UV-vis spectrofluorometer, which is acquired from reflectance spectra of PS/GQDs thin film in **Fig. 5b**. The calculated peaks closely matched with experimental test wavelengths.

7. Electron microscopy image of polystyrene nanoparticles with/without GQDs

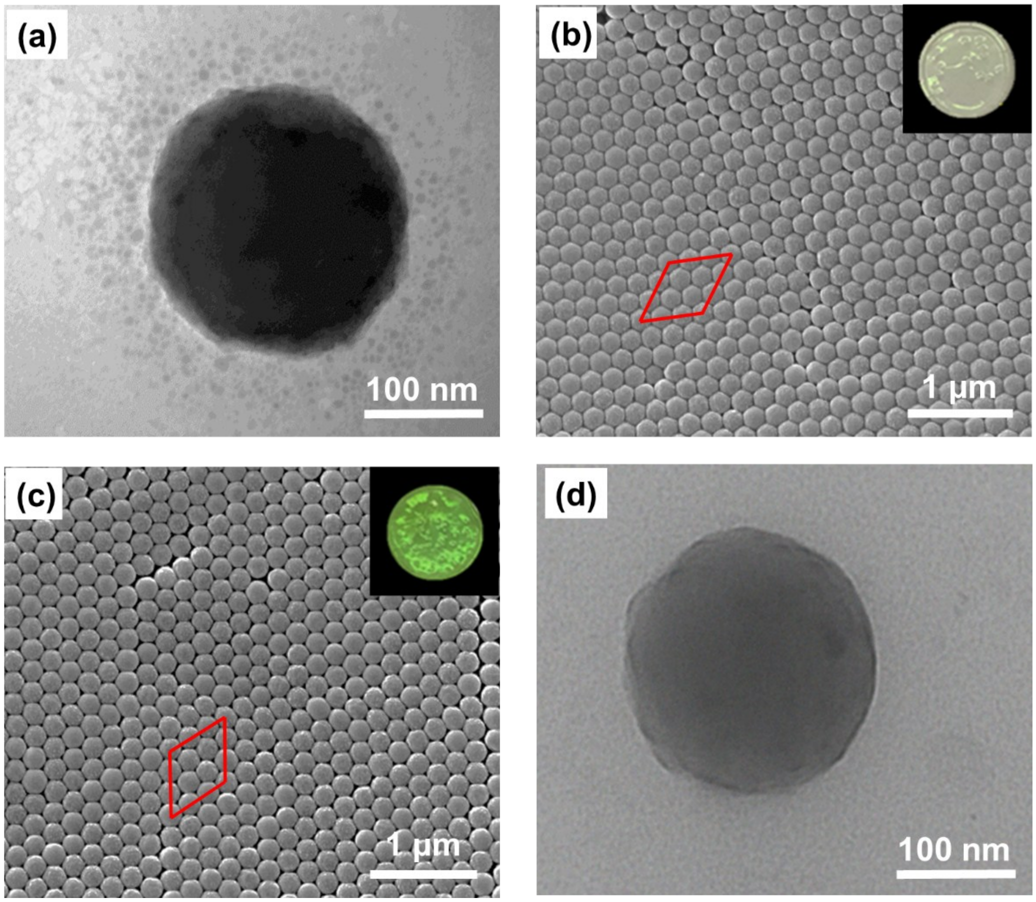

Fig. S7. Electron microscopy image of PS nanoparticles and PS nanoparticles with GQDs additives. (a) HRTEM image of PS/GQDs photonic crystals. (size of PS is 214 nm, ratio of GQDs-7 to PS is 1 wt%). (b) SEM image of 214 nm PS nanoparticles. (c) SEM image of PS/GQDs photonic crystals. The inset of (b) and (c) are their corresponding thin film photographs. (d) HRTEM image of PS photonic crystals. (size of PS is 214 nm).

Fig. S7a showed the single PS nanoparticle with GQDs. The SEM image of pure PS and PS/GQDs were shown on **Fig. S7b** and **S7c**. 1 wt% GQDs increment into PS greatly improved the color of photonic crystals from pale green to bright green. The periodic lattice structure of close packed PS nanoparticles did not change after GQDs entering the void space of colloidal photonic crystals. It was confirmed by measuring distance between PS particles (shown on red parallelogram) through ImageJ analysis software. **Fig. S7d** showed a single pure PS nanoparticle. It could clearly find out the difference with/without GQDs between **Fig. S7a** and **Fig. S7d**.

8. Zeta potential test for PS and GQD nanoparticles.

Table S3. Zeta Potential of PS, GQDs and PS/GQDs

Group 1	zeta potential (mV)		Group 2	zeta potential (mV)
PS 192nm	-38.8		PS 192/GQDs-3	-38.9
PS 214nm	-37.2		PS 214/GQDs-3	-37.8
PS 274nm	-39.5		PS 274/GQDs-3	-37.5
PS 396nm	-40.3		PS 396/GQDs-3	-38.4
Group 3	zeta potential (mV)		**Group 4**	zeta potential (mV)
GQDs-3	1.2		PS192/GQDs-3	-39.2
GQDs-5	0.3		PS192/GQDs-5	-38.6
GQDs-7	0.8		PS192/GQDs-7	-39

Four groups of zeta potential of PS, GQDs and PS/GQDs were tested and as shown in **Table S3**. From **Table S3**, zeta potential of pure PS nanoparticle is negative (Group 1), and zeta potential of GQDs is positive (Group 3). The PS/GQDs composites all have a negative zeta potential (Group 2 and Group4).

9. Raman spectroscopy of GQDs

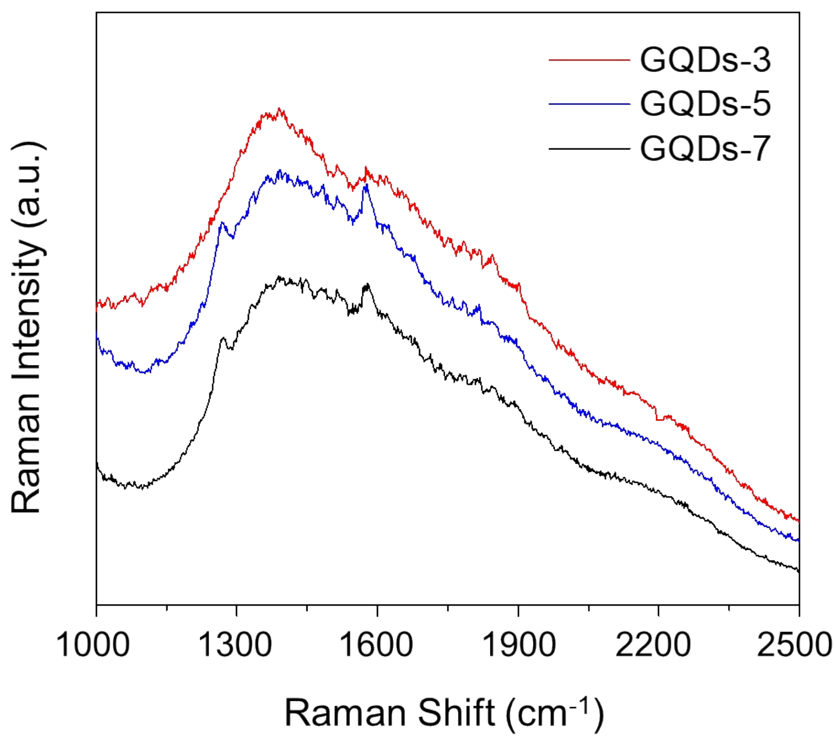

Fig. S8. Raman spectroscopy for various GQDs.

Fig. S8 shows the Raman spectra of GQDs-3, GQDs-5 and GQDs-7. G band at around 1580

cm^{-1} was found and D band at around 1350 cm^{-1} was not obvious to see.[1] We considered that since our GQDs have very high fluorescence intensity, the high intensity of fluorescence will largely affect the Raman spectra and overlap the D band and G band peak. There is also other research work talking about the fluorescence affecting Raman spectra.[2]

Reference

1. X. Ma, Q. Xiang, Y. Liao, T. Wen and H. Zhang, Applied Surface Science, 2018, 457, 846-855.

2. Zhu, S., Meng, Q., Wang, L., Zhang, J., Song, Y., Jin, H., ... & Yang, Angewandte Chemie, 2013, 125(14), 4045-4049