Supporting Information

Emission States Variation of Single Graphene Quantum Dots

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Confocal microscope

Fluorescence spectra were measured using an Andor SR 303i spectrograph and a CCD camera (Andor iXon DU897 BV). Fluorescence lifetime measurements were performed with a custom-built confocal microscope equipped with an objective lens of high numerical aperture (Apo N, 60×/1.49 NA oil immersion, Olympus). A white light laser system (Fianium SC400-4-20) with a tunable filter (AOTFnC-400.650-TN) served as excitation source. Excitation wavelength for all the single particle measurements was 485 nm; excitation power was 3 µW before the objective lens. Collected fluorescence was focused onto the active area of a single photon detection module (MPD series, PDM). Data acquisition was accomplished with a multichannel picosecond event timer (PicoQuant HydraHarp 400). Photon arrival times were histogrammed (bin width of 32 ps) for obtaining fluorescence decay curves. Generation of a radially and azimuthally polarized laser beams was done using a liquid crystal polarization converter from ARCoptix. The fluorescence correlation spectroscopy (FCS) measurements were done using the same experimental parameters as for the single particle measurements.

Single particle samples preparation

For the single particle studies on a glass-air interface, 20 µl of aqueous solution of GQDs was spin-coated on clean glass cover slide at 6000 rounds per minute rotation speed. For the studies of particle in a polymer matrix, a 20 µl droplet of 1% PVA (Polyvinylalcohol 18-88, Sigma Aldrich) with GQDs was spin-coated on clean glass cover slide at 6000 rounds per minute rotation speed. Control measurements both on glass-air interface and polymer matrix showed a two orders of magnitudes lower signal as compared to the luminescence of single GQDs (see Figure S1).

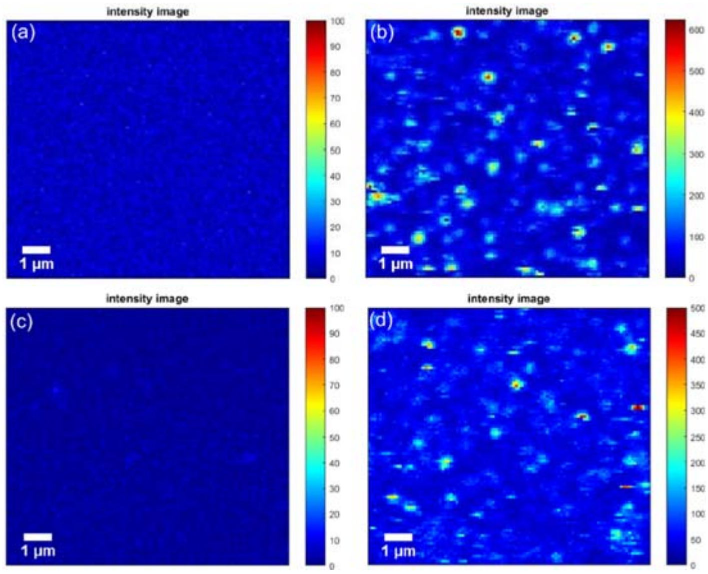

Figure S1. Control measurements of the samples used for single particle measurements. (a) a clean glass-air interface without particles; (b) a clean glass-air interface with GQDs spin-coated; (c) a polymer film spin-coated on a glass substrate without GQDs; (d) a polymer film spin-coated on a glass substrate together with GQDs.

Single particle polarization measurements

Figure S2 shows excitation patterns of the same single GQD measured by scanning it through the focal area of a radially and azimuthally polarized laser beam. Figure S3 shows excitation patterns of a single quantum emitter that has different a dimensionality and orientation of transition dipoles. The patterns were calculated according to the scheme shown on top of the figure and according to the experimental conditions and parameters of the microscope that were used in the measurements. The striking difference of the excitation patterns allows one to unambiguously distinguish different dimensionalities and orientations of transition dipoles. It should be noted that in contrast to other techniques, such as rotation of a linear polarizer in front of a detector or use of only the azimuthal mode, these techniques allow one to determine not only orientation of transition dipoles within the sample plane but also the out-of-plane tilt of a dipole. Comparison of the measured and simulated single particle patterns allow us to attribute the emission to a fixed linear transition dipole.

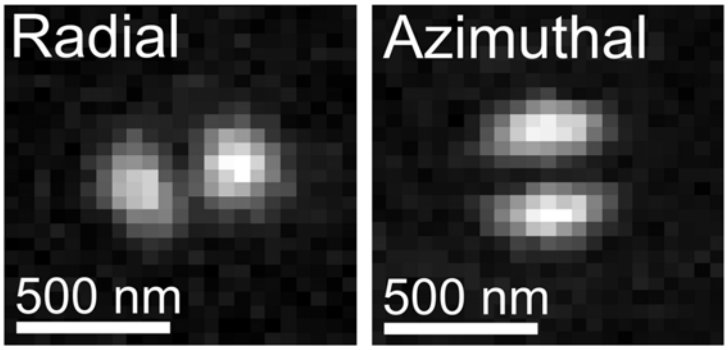

Figure S2. Single particle images measured by scanning it on a glass-air interface through the focal area of a radially (left) and azimuthally (right) polarized laser beams, respectively. Except a different transition dipole orientation, all the single particle patterns were identical for all the GQDs measured, both on glass-air interface and in a polymer matrix.

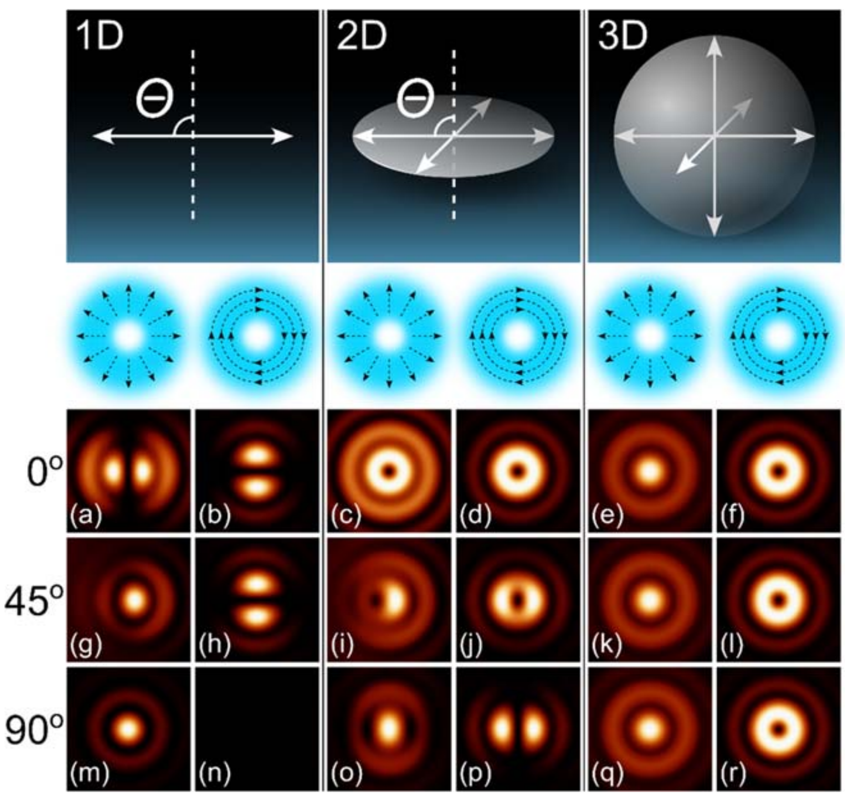

Figure S3. Theoretical excitation (a–r) patterns of a single quantum emitter that has various orientations and degeneracies of transition dipole moments. The patterns were modeled according to the schemes shown on top of the figure for 485 nm excitation wavelength.

Single particle spectroscopy

Figure S4 shows representative examples of single GQDs spectra measured on a glass-air interface and in a polymer matrix. The spectra measured on a glass-air interface are in average more intense and their bands are narrower as compared to the data obtained in a polymer matrix.

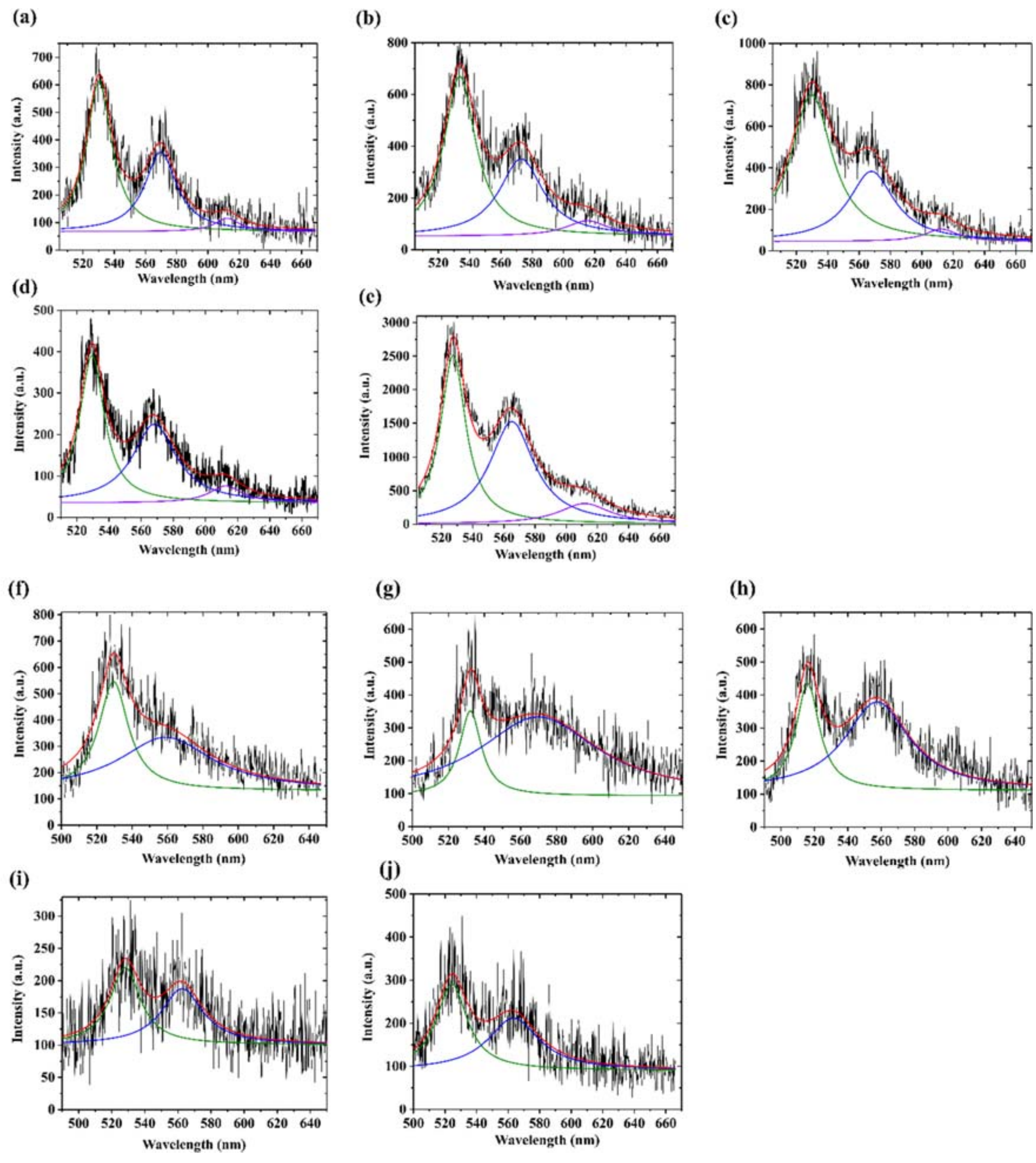

Figure S4. Fluorescence spectra of single graphene quantum dots placed on a glass-air interface (a-e) and in a polymer film (f-j). Black curves are measured data; red curves are total fits that contain three (a-e) and two (f-j) Lorentzian functions.

Photostability of graphene quantum dots

The total number of photons detected from a single particle did not show any clear dependence on whether GQDs were placed on a glass-air interface or in a polymer matrix, see Figure S5.

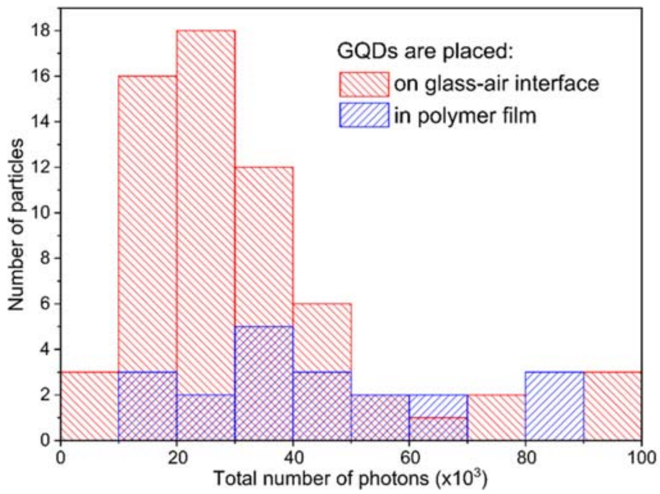

Figure S5. The total number of photons detected from single graphene quantum dots placed on a glass-air interface and in a polymer film.