Supporting information

Assembly of graphene nanoflake-quantum dot hybrids in aqueous solution and their performance in light-harvesting applications

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Contents

1. Preparation of graphene nanoflakes

Graphene nanoflakes (GNFs) were synthetized according to a published procedure:[1] 1.00 g of MWCNT (3 to 15 walls, 5 – 20 nm outer diameter and 2 – 6 nm inner diameter and 1 to 10 µm in length; purchased from Bayer Materials Science) were ultrasonicated in a 100 mL mixture of 3:1 vol% conc. sulfuric acid (95-97% w/w) and conc. nitric acid (70% w/w) for 30 minutes. The reaction mixture was heated for 2 h at 100°C, cooled to room temperature and diluted three-fold with deionised water. The black dispersion was filtered through a 200 nm track-etched polycarbonate membrane and the black residue on the membrane was discarded. The black filtrate was neutralised with KOH and the white salt precipitate (consisting mainly of K_2SO_4) was removed by filtration. The black filtrate was reacidified with dilute nitric acid until pH 2 and then dialysed against high-purity Milli-Q water using a SpectraPor 3 regenerated cellulose dialysis membrane (Spectrum laboratories, MWCO 3.5 kDa). Once the conductivity of the surrounding water was below 5 µS cm^{-1} the dispersion was passed over a cation exchange resin (Amberlite IR120, Sigma-Aldrich), dialysed once more and freeze dried to obtain 160 mg of brown-black GNFs.

2. Sample characterisation

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha XPS machine with a monochromated Al Kα source (E = 1486.6 eV), a double focusing 180 degree hemisphere analyser of 125 mm radius and detected with a 18 channel position-sensitive detector. A dual-beam flood gun (electrons and argon ions) was used to compensate for charge accumulation on the measured surfaces. The GNFs were pressed onto an indium substrate before analysis. Survey scans were collected 3 times with a resolution of 1 eV and all elemental regions were scanned 10 times with a resolution of 0.1 eV. All scans were recorded with a 50 ms dwell time and 400 µm spot size. Peak fitting of the C1s region was performed using XPSPEAK version 4.1 software using a Shirley background function and voigt functions for the fitted peaks.

Atomic force microscopy (AFM)

Samples were imaged under ambient conditions with a Bruker Dimension Icon microscope, with a NanoScope IV control unit. Tapping-mode AFM imaging was performed with SCANASYSTAIR tips (Bruker, spring constant 0.4 N m^{-1}). Images were analysed with NanoScope Analysis (version 1.5, Bruker) software. For adhesion images, the tip-sample adhesion force was determined from the difference between the zero force and the minimum force experienced during tip retraction.

UV-Vis absorbance spectroscopy

UV-Vis spectra were collected with a Perkin Elmer Lambda 35 spectrometer. Samples were measured in a 45 μL volume Hellma cuvette, light path 3 x 3 mm.

Stationary photoluminescence spectroscopy

Stationary photoluminescence spectra were recorded with an Agilent Technologies, Cary Eclipse Fluorescence Spectrophotometer. Samples were excited at 420 nm, slit width 5 nm, and spectra where acquired between 400 and 800 nm.

Transmission electron microscopy (TEM)

Samples for TEM imaging were prepared by drop casting onto TEM grids and dried in a desiccator. The grids were then rinsed with water and dried again in a desiccator. A JEOL 2010 microscopy was used to collected TEM images operating at 200 KeV.

Time-resolved fluorescence spectroscopy

Time-resolved measurements were carried out on solutions of QDs alone and GNF-QD hybrids. The following experimental setup was employed: Laser light was generated by a Continuum Surelite (SLI-10) laser, the beam then passes through an optical parametric oscillator (OPO: Continuum Panther). Tuning the laser output at a specific wavelength is achieved using a computer program. The beam passes through a series of lenses and it is focused onto the sample. The photoluminescence is then collected and collimated onto a Jobin Yvon Horiba Triax 550 spectrometer. A nitrogen-cooled photomultiplier tube (PMT) (Photocool PC176TSCE005) is used to detect and multiply the signal collected from the spectrometer. The response from the PMT is then sent to an oscilloscope (LeCroy waverunner LT372). The photoluminescence spectra and lifetime data is recorded by a connected

computer. Samples were excited at 420 nm and the decay emission was monitored at 594 nm which corresponds to the maximum emission of QD and GNF, respectively.

Raman spectroscopy

Samples for Raman spectra measurements were prepared by drop casting the solutions of QDs and GNF-QD hybrids onto glass slides (VWR microscope cover glasses) previously cleaned with a plasma cleaner for 5 min (PDC- 32G-2 (230V) Plasma Cleaner, Harrick Plasma) and dried in air. Raman spectra were acquired with a Renishaw InVia spectrometer equipped with a 514.5 nm argon-ion laser using a 50-fold magnification objective. Eight spectra were accumulated for 20 seconds each and coadded to give the final spectra. Finally, the Raman shifts of the spectra were calibrated against the 520.7 cm^{-1} mode of a silicon wafer.

Confocal microscopy

Samples for confocal microscopy were prepared by drop casting the solutions of QDs and GNF-QD hybrids onto glass slides (VWR microscope cover glasses) previously cleaned with a plasma cleaner for 5 min (PDC- 32G-2 (230V) Plasma Cleaner, Harrick Plasma), for few minutes then rinsed with water and ethanol and then blown dry in air. Confocal microscopy was carried out on an LSM 710 ELYRA PS.1 and the QDs were excited using a 488 nm laser. Time series of the nanohybrids were taken for 300 s with an exposure time of 100 ms.

3. Characterisation of as-made GNFs

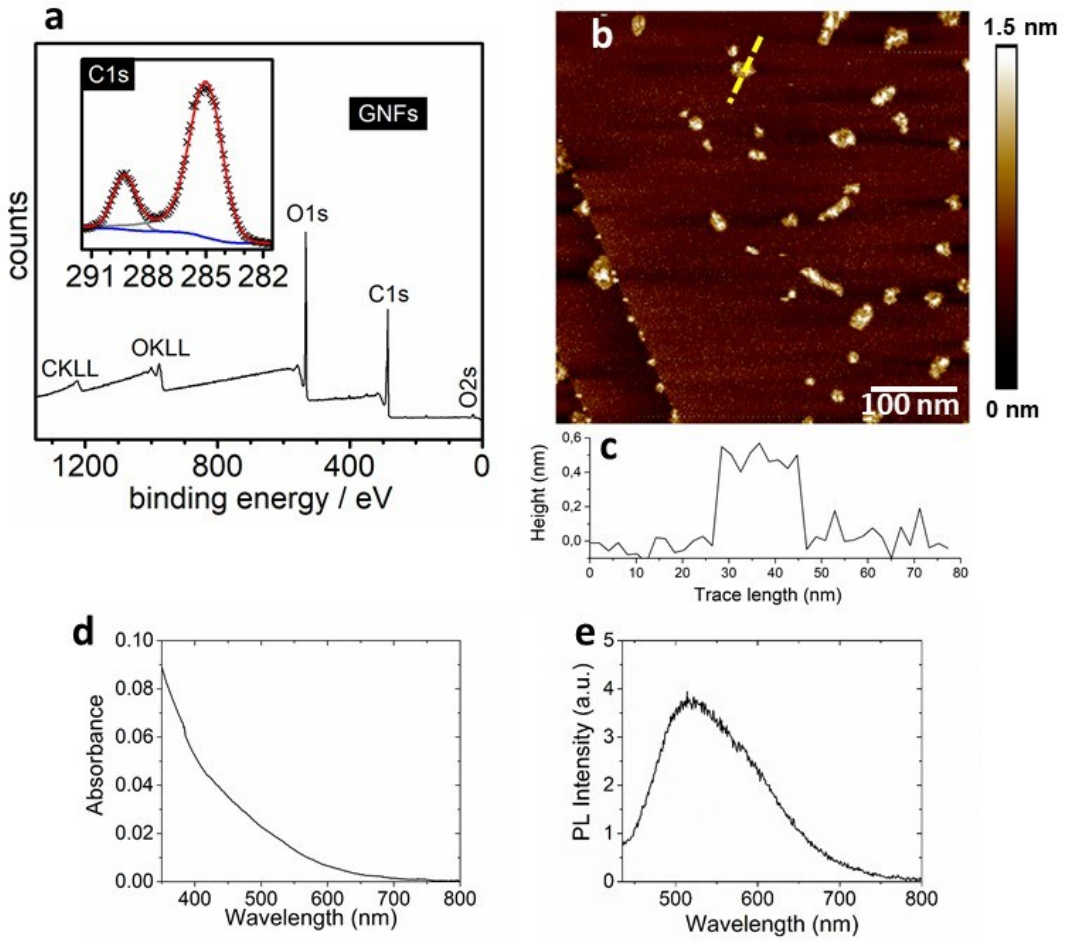


Figure S1 (a) XPS spectrum of as-made GNFs and high-resolution C1s region (inset). (b) AFM topographical image of as-made GNFs. (c) Height profile of a single graphene nanoflake corresponding to the yellow dashed line in (b). GNFs show an average height of 0.5 nm and average lateral dimensions of 20 by 30 nm. (d) UV-vis spectrum of as-made GNFs (GNFs concentration about 0.01 mg/ml, light path 3 mm). (e) Stationary photoluminescence of as-made GNFs.

4. Assembly

Graphene nanoflakes were dispersed in water by mixing at a concentration of 0.1 – 1 mg/ml. CdSe/ZnS core/shell quantum dots functionalized with amino groups were purchased from Ocean Nanotech (4 nm core, 2 nm shell). QD-GNF nanohybrids were formed in aqueous solution by mixing equal volumes of water solutions of nanoflakes (0.4 mg/ml) and QDs (3 μM) and allowed for reaction overnight under continuous stirring. To study the effect of pH on the coupling reaction formation, equal volumes of GNFs and QDs dispersed in the

appropriate buffer (MES 0.1M pH 4.7; PIPES 10 mM pH 6.1, ThermoScientific BupH Phosphate Buffered Saline pH 7; HEPES buffer 10mM pH 8; sodium carbonate 30mM-sodium bicarbonate 70 mM buffer pH9.5) were mixed and allowed to react overnight under continuous stirring. To study the effect of polarity on the coupling reaction formation, equal volumes of GNFs and QDs dispersed in different ethanol / water volume ratios (0/10, 1/10, 3/10, 5/10, 7/10, 9/10 and 10/10) were mixed and allowed to react overnight under continuous stirring.

5. Casting Procedure

Adopting drop cast techniques, solutions were cast onto freshly cleaned HOPG surfaces for few minutes and then washed with ethanol and ultra-pure H_2O followed by blow drying with nitrogen.

6. Atomic force microscopy (AFM) of GNF-quantum dot hybrids

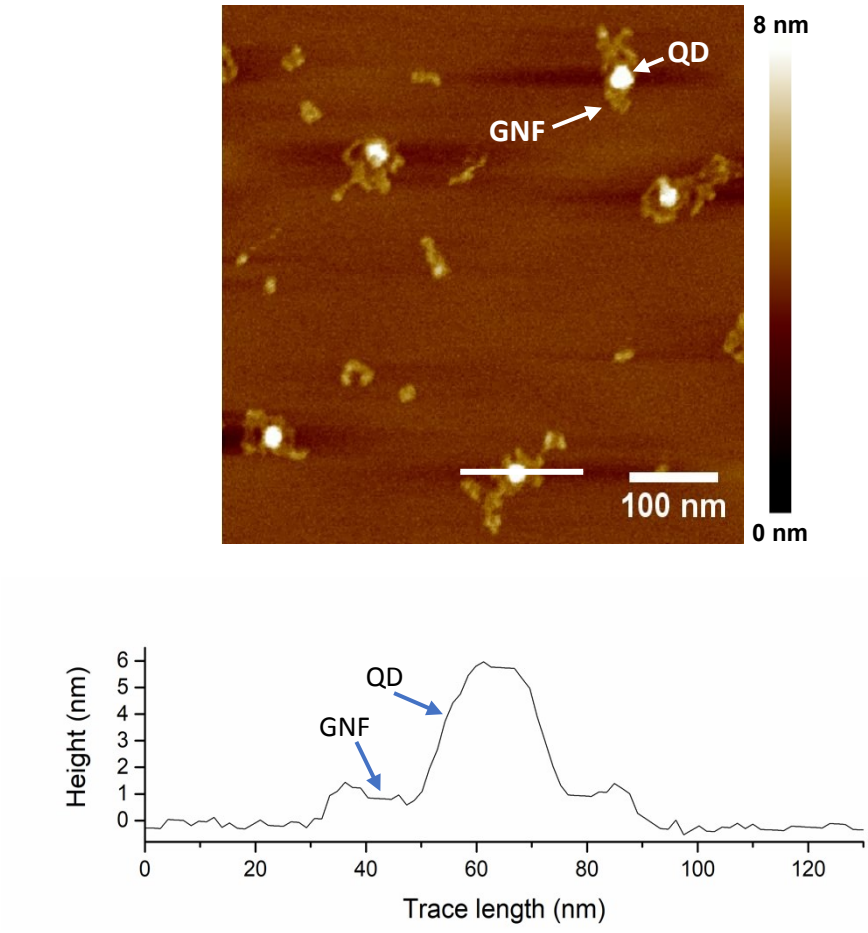


Figure S2 AFM topography image (top) and height analysis of GNF-QD nanohybrids (bottom). The heights measured are in line with the height of individual QDs and graphene nanoflakes.

7. Transmission electron microscopy (TEM) of GNF-quantum dot hybrids

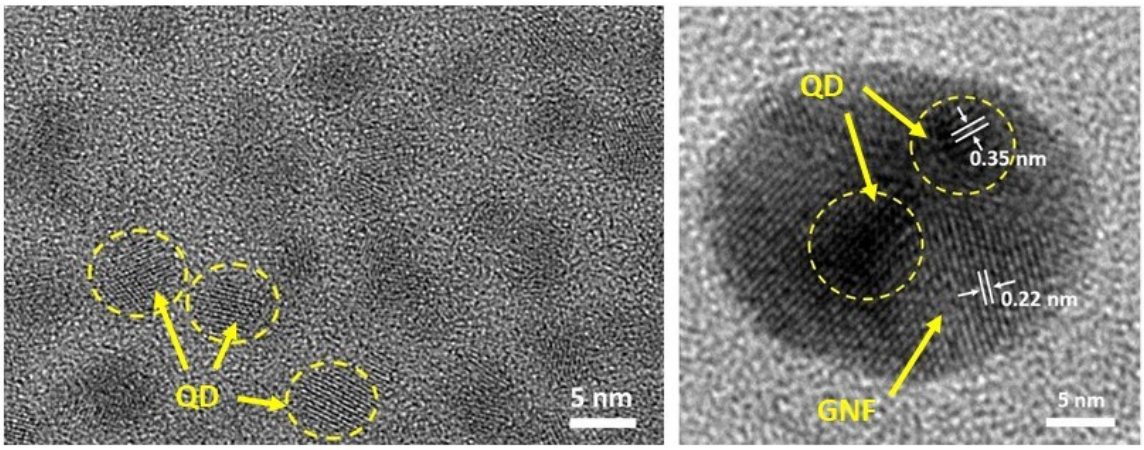


Figure S3 TEM images of (left) pristine QDs and (right) QD-GNF hybrids. The arrows highlight the lattice interplane distances for GNFs (0.22 nm) and QDs (0.35 nm).

8. Stationary photoluminescence

In order to be able to compare the PL intensities and hence the PL quenching, each pair of samples of GNF-QD hybrids and pristine QDs, each in different condition of pH and solvent polarity were processed in exactly the same way, with the only difference being the presence or absence of GNFs. In all cases, the same amounts of QDs have been exposed to the light and the quenching can only be ascribed to the coupling of QDs covalently attached to the GNF. The quenching factor was calculated as follows:

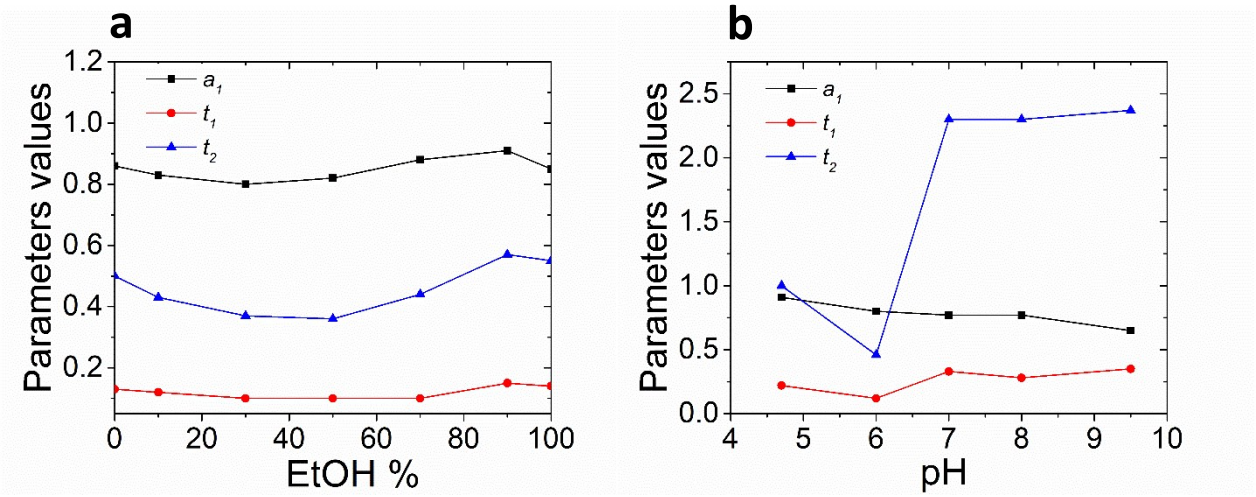
$$Quenching = \left(1 - \frac{PL_{max}^{GNF-QD}}{PL_{max}^{QD}}\right) \times 100 \quad (1)$$

Where PL_{max}^{QD} and $PL_{max}^{QD\text{-}GNF}$ are the photoluminescence maxima of the QD and GNF-QD for each pair of samples at 594 nm.

9. Time-resolved measurements

The PL traces were fitted with a biexponential function according to the following equation:

$$PL(t) = a_1 e^{-\frac{t}{\tau_1}} + a_2 e^{-\frac{t}{\tau_2}} \quad (2)$$



c

% of EtOH	a_1	t_1	t_2
0	0.86	0.13	0.50
10	0.83	0.12	0.43
30	0.80	0.10	0.37
50	0.82	0.10	0.36
70	0.88	0.10	0.44
90	0.91	0.15	0.57
100	0.85	0.14	0.55

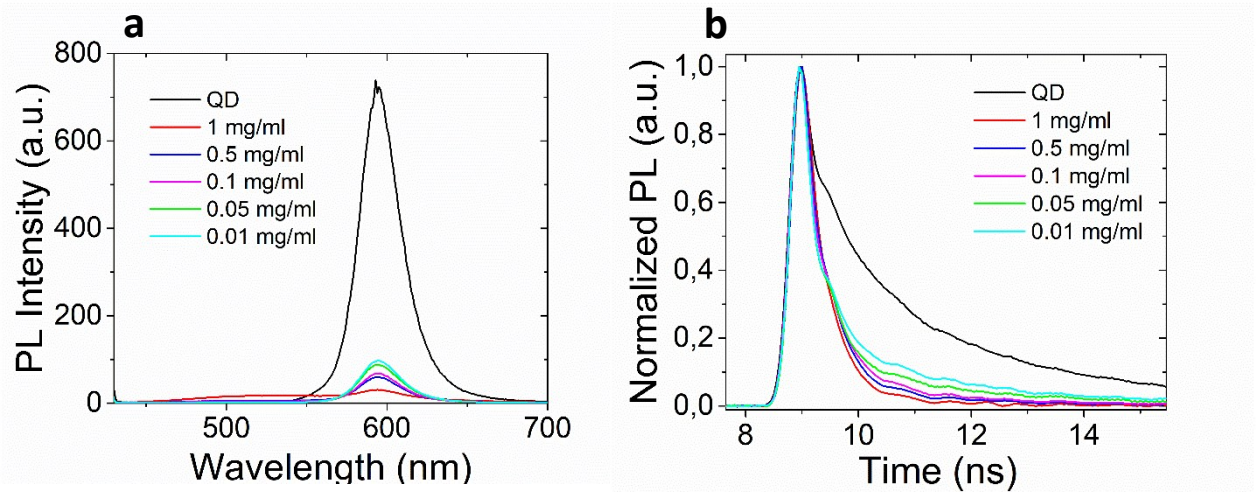
d

pH	a_1	t_1	t_2
4.7	0.91	0.22	1.01
6	0.80	0.12	0.46
7	0.77	0.33	2.30
8	0.77	0.28	2.30
9.5	0.65	0.35	2.37

Figure S4 Fitting parameters of the photoluminescence decay traces of GNF-QD hybrids at (a) different solvent polarity and (b) different pH. The corresponding values are listed respectively in (c) and (d).

The time-resolved fitting parameters do not vary significantly by changing the polarity of the solvent in line with the PL quenching observed. Moreover, at different pH, in all cases, the decays present a more pronounced monoexponential decay and shorter lifetimes compared to the free QDs, indicating the occurrence of coupling but with different efficiencies at different pH. In particular, we observe the shortest lifetimes at pH 6, confirming that this is the best pH condition for the coupling (in line with the PL quenching shown in Figure 2b). At

pH 4.7 the monoexponential decay is more pronounced, but both lifetimes are longer than the corresponding value at pH 6. Furthermore, for pH greater than 6 the longer lifetime t_2 increases significantly (again in line with the quenching shown in Figure 2b).



c

GNF in mg/ml	quenching
1	95
0.5	91
0.1	90
0.05	87
0.01	86

d

GNF in mg/ml	a_1	t_1	t_2
1	0.86	0.14	0.51
0.5	0.81	0.15	0.57
0.1	0.82	0.18	0.61
0.05	0.79	0.38	2.51
0.01	0.60	0.34	2.50

Figure S5 (a) Stationary photoluminescence spectra and (b) time-resolved photoluminescence spectra of QD-GNF solutions at different concentrations of nanoflakes. (c) Corresponding fitting parameters for the decays at different GNF concentrations.

Upon increasing the GNFs concentration from 0.01 to 1 mg ml^{-1}, as expected we observe a progressive quenching of QDs static PL. Additionally, both the lifetimes were observed to progressively shorten, from time-resolved PL investigations. This overall concentration-dependent behaviour is in line with previously reported studies on similar systems.[2,3]

10. Raman spectroscopy

In order to assess the down shifts of the D and G peaks in the presence of QDs, a baseline correction was applied to the raw data as shown in Figure S6. The broad peak at around 2500 cm^{-1} corresponds to the QD PL emission.

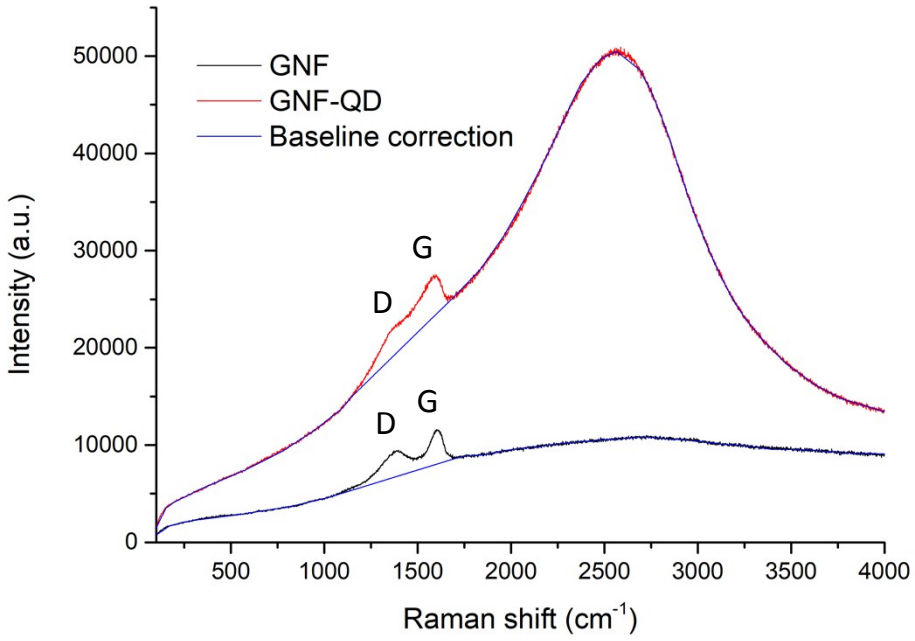


Figure S6 Raman spectra of pristine GNFs (black) and GNF-QD hybrids (red). The blue lines were used as baseline correction to evaluate the peak shits of the G and D bands.

11. Confocal Fluorescence Microscopy and blinking analysis

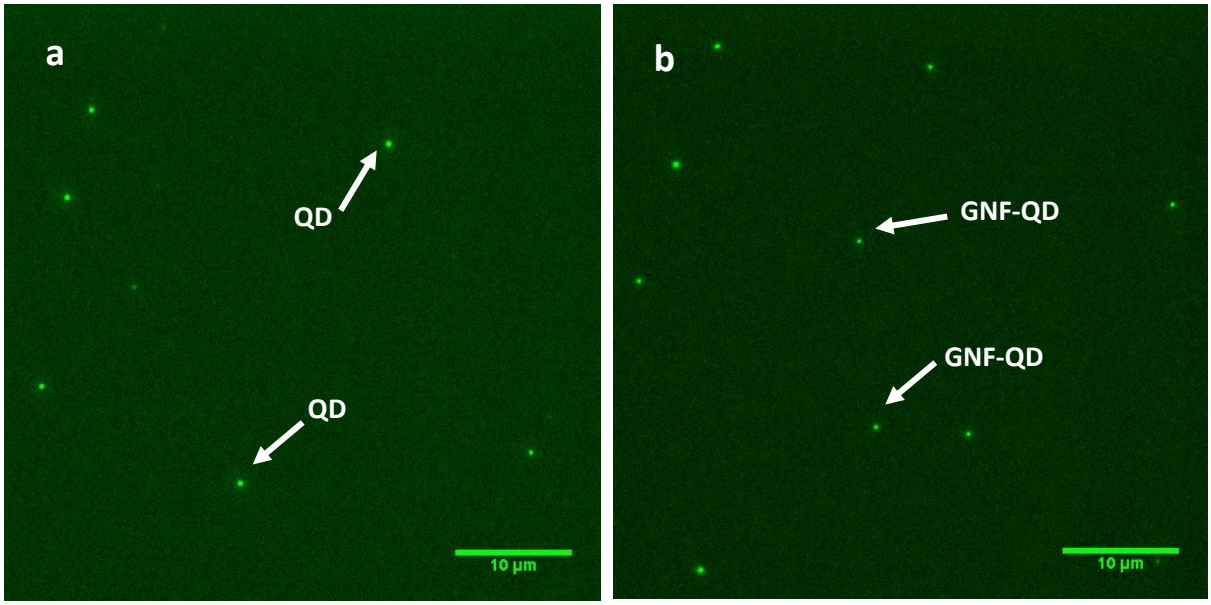


Figure S7 Representative image frames taken from the movies used to study the PL blinking of (a) QDs and (b) GNF-QD hybrids.

The probability distributions (see Figure 4e) were calculated according to published procedures.[4,5] Data were first analysed with ImageJ to extract luminescence intensity data as a function of time and then processed with OriginLab9 and MATLAB to generate the probability distributions. To determine the threshold intensity that separate on and off states, the distribution of the PL intensities was fit by a sum of two Gaussian functions. The point where these two Gaussians cross was taken as the threshold intensity.

The OFF periods for an experiment are binned into a histogram with 100 ms bin width. The cumulative data from all QDs blinking in a given experiment are treated as an ensemble. The probability densities for the off periods $P^{off}(t_i)$ is determined by Equation 3:

$$P^{OFF}(t_i) = \frac{N(t_i)}{N_{tot}} \times \frac{1}{\Delta t_{avg}} \quad (3)$$

where $N(t_i)$ is the number of OFF events within the time bin t_i , N_{tot} is total number of OFF events and Δt_{avg} is the average time between neighbouring events. The data were then plotted in log-log space as seen in Figure 4e and fitted with a truncated power law model according to Equation 4:

$$P_{OFF} = B_{OFF} t^{-m_{OFF}} exp(-T_{OFF} t) \quad (4)$$

Where B_{OFF} is the amplitude, m_{OFF} is the power-law exponent and T_{OFF} is the saturation rate.

12. Solar cell fabrication

Solar cells were assembled using a premade kit from Greatcell solar consisting of TiO_2-coated transparent glass electrodes and platinum coated counter electrodes. Pristine QD and GNF-QD hybrids (0.2 mg ml^{-1} of GNF and 2 uM of QD) were drop casted on the TiO_2 coated electrodes on a hot plate at 40°C, heated for 30 minutes under ambient conditions and then under vacuum at 40°C for 3 hours. The same amount of QDs was used for all the devices tested. Solar cells were assembled in a sandwich configuration where parafilm was used to

create a chamber between the two electrodes in order to accommodate the electrolyte solution (0.1 M Na_2S). The active area was 88 mm^2.

13. Photocurrent measurements

Photocurrent measurements of the solar cell have been carried out with an irradiation from an ABET Sun Simulator AAA with AM1.5 filter. The solar cells were irradiated at 1 sun (100 mW cm^{-2}). The irradiation was calibrated with a reference Silicon solar cell. The photo-response of solar cells has been measured using an oscilloscope GW Instek GDS-2062.

14. References

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