Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Easy Extraction of Water-soluble Graphene Quantum Dots for Light Emitting Diodes

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Synthesis of graphene quantum dots (GQDs):

Initially graphene oxide sheets (GOS) were synthesized from graphite powder by using modified Hummers' method.[1, 2] The GQDs were further synthesized from GOSs by a simple one step hydrothermal process. For the synthesis of GQDs, 5 ml of GOS solution (1 mg/1 ml loading), 5 ml of de-ionized water and 3 ml of ammonia solution were added together in a beaker and continuously stirred for 30 minutes. The resulting mixture was transferred into Teflon - lined autoclave (50 mL) and heated at 150 °C in a hot oven for 5 hours under hydrothermal conditions. The solution was naturally brought down to room temperature and subsequently large fragments retained within the suspension were filtered out by using a 0.02 µm anopore inorganic membrane (Anodisc TM, Whatman). The required GQDs were present in the supernatant (filtrate). The collected transparent supernatant was heated at 80-90 ºC for 1 hour to vaporize the excess ammonia. Then, the resultant supernatant was ultra-filtered through centrifugal filter device with a 10 k Da molecular weight cut-off membrane (Saretorious) to filter out the unwanted small fragments. The final transparent solution consisting of GQDs was collected and used for further characterization.

Characterization:

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) measurements were carried out using a JEOL JEM-2010 microscope with an accelerating voltage of 200 KV. UV-vis absorption and photoluminescence (PL) spectra were recorded with a Shimadzu UV-2550 spectrometer and a NanoLog spectrofluorometer (HORIBA Jobin Yvon) respectively. Time decay profiles were carried out by Horiba Jobin Yvon Fluromax-4 (picosecond diode laser in IBH Fluorocube apparatus JY-IBH-5000M). The powder-GQD samples were obtained by using the EYELA - Rotary Evaporator system. The current - voltage (I-V) measurements of GQD-light emitting diode (LED) devices were carried out using a Keithley 2420 source-measure unit. The electroluminescence (EL) spectra of the GQD-LED devices were recorded using a NanoLog spectrofluorometer fitted with an additional optical fibre module. The 1931 Commission Internationale de l'éclairage (CIE) chromaticity coordinates for corresponding EL spectra were calculated by “GOCIE” software.

Extraction of powder - GQD samples:

A simple one step rotary evaporation technique was utilized to separate the GQDs from water phase. The water from the GQD sample was evaporated under reduced pressure of ~ 10^{-1} mbar and at an elevated temperature of ~ 45-55 $^{\circ}$C. The rotary evaporation technique is very rapid (~10 minutes) to complete the evaporation and drying process. The collected powder-GQD samples were redispersed into ethanol solution and ultrasonicated for 10 minutes. The well dispersed GQDs-ethanol solution was used for thin film preparation and device fabrication.

Experimental Process:

In the process of converting the water-GQDs into powder-GQDs, initially ~ 8 ml of water-GQDs solution was taken into one round neck bottom flask (~ 25 ml capacity) and fitted to the rotary evaporator. A vacuum system is employed to substantially reduce the pressure within the evaporator system. A water bath with temperature controller is used to heat the sample (round neck bottom flask). Water is removed in the form of vapor at a temperature of ~ 45-55 °C under reduced pressure. The condenser (a coil circulated with cooled water) cools the gaseous solvent, which returns it to its liquid phase. Additional flask at the bottom of the condenser is used to collect the solvent after the vapor re-condenses. The solvent can be “trapped” as a liquid in the additional flask attached to the condenser. Finally, the powder-GQDs were collected from round neck bottom flask.

Fabrication of GQD-LED devices:

GQD-LED devices were fabricated on patterned indium tin oxide (ITO) glass substrates by spin coating technique. Initially, the patterned ITOs were cleaned sequentially using soap solution, de-ionized water, acetone, ethanol and finally with 2-propanol. In each step during the cleaning process, the ITO substrates were ultrasonicated for 10 minutes. The cleaned ITO substrates were dried in oven at 60 °C for overnight. A thin layer of Poly (ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) hole injection layer was deposited via spin-coating onto cleaned ITOs at ~ 5000 rpm for 1 minute using an aqueous solution. The films were annealed in N_2 atmosphere at 150 °C for 30 minutes to obtain a uniform layer. On top of the PEDOT:PSS thin film, organic hole-transport layer poly-TPD in chloroform solution with a loading of 10 mg/ml was spin-coated at a speed of ~3000 rpm for 30 seconds. The films were dried at 110 °C for 1 hour in nitrogen environment. Subsequently, the dried powder-GQD samples dissolved in ethanol solution with a loading of ~10 mg/ml and ultrasonicated for 10 minutes to obtain well dispersed GQD-ethanol solution. Emissive GQDs were used as the active light emitting layer within the LED device structure. A thin layer of GQDs was deposited on top of poly-TPD layer from the GQD-ethanol solution by spin-coating at ~2000 rpm for 30 seconds, followed by drying under N_2 atmosphere at 90 °C for 30 minutes. The ZnO nanoparticles were used as electron injecting layer and spin-coated on top of the GQDs layer with a loading of 30 mg/ml in chloroform solution at a speed of ~2000 rpm for 30 seconds and annealed at 120 °C for 30 minutes under N_2 flow. Finally, aluminium (Al) electrodes (cathodes) were thermally evaporated through a shadow mask without breaking the vacuum in a hind-vacuum thermal evaporation system.

Current density -voltage characteristics of GQD-LEDs:

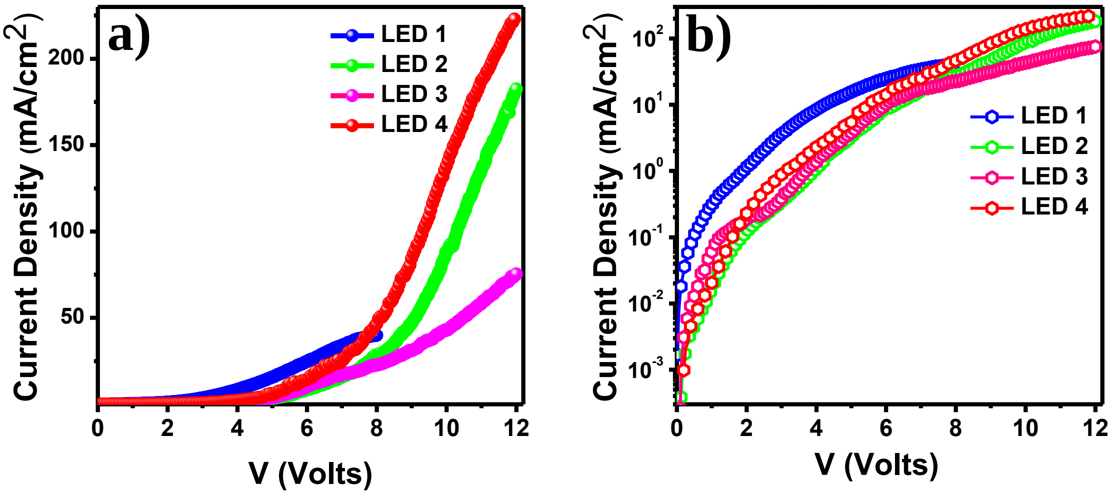

Figure S1. Current density - voltage (J-V) characteristics of GQD-LED devices measured at ambient conditions. a) J-V curves in linear scale and b) J-V curves in logarithmic scale for GQD-LED devices.

Comparison of EL and PL spectrum of GQDs:

We have compared the EL spectrum of GQD-LED device with the PL spectrum of the GQDs. The corresponding CIE coordinates calculated using GOCIE software are presented in Figure S2a. The CIE chromaticity coordinates of the EL spectrum at (0.16, 0.34) of GQD-LED nearly overlapping with the CIE chromaticity coordinates at (0.17, 0.28) of GQDs PL spectrum confirming that the EL is originated from GQD layers of the LED device. Figure S2b shows the schematic representation of possible charge carrier transition mechanisms leading to PL and EL spectra. Therefore, the transitions of charge carriers are taking place between different energy levels (through different radiative recombination channels) within the GQDs resulting in the color tunable PL and EL behavior (Figure S2b).

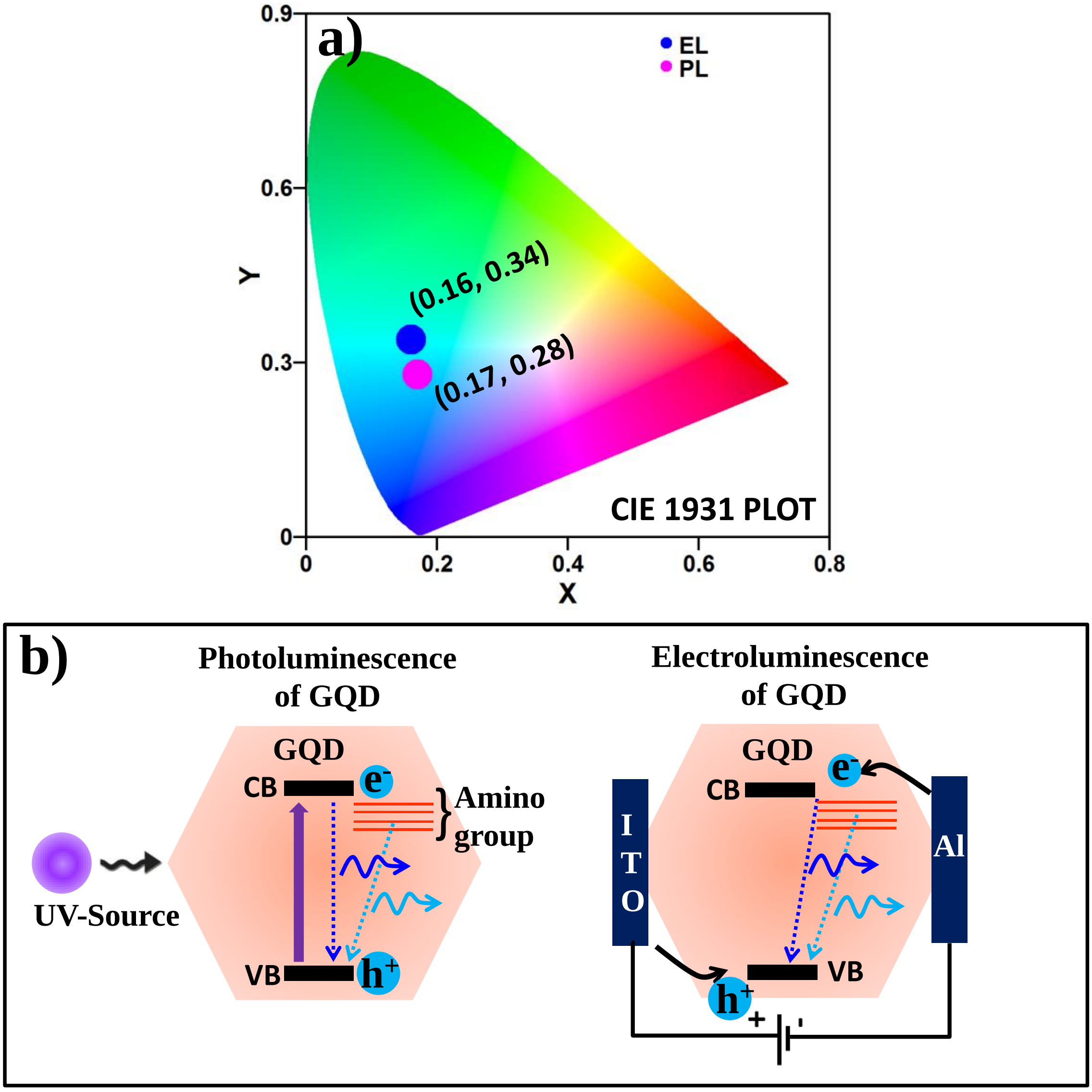

Figure S2. a) Comparison of calculated CIE chromaticity coordinates corresponding to EL spectrum of GQD-LED device operated at a bias voltage of ~ 9 V and PL spectrum of GQDs at the excitation wavelength of ~ 380 nm. b) Schemes showing the possible PL (left) and EL (right) mechanisms in GQDs.

References:

1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

2 H. Tetsuka, R. Asahi, A. Nagoya, K. Okamoto, I. Tajima, R. Ohta and A. Okamoto, *Adv. Mater.*, 2012, **24**, 5333.