Thiolated Graphene – a New Platform for anchoring CdSe QD for hybrid heterostructures

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Supporting Information

Detailed synthetic and Characterization Procedure:

0.1 g GO was suspended in water using sonication for 15 min followed by reduction with $NaBH_4$ (1:3 wt. ratio) for 12 h to obtain chemically converted graphene (CCG) or reduced graphene oxide (RGO). After that, the mixture was filtered through 0.4 µm PTFE filter paper and washed thoroughly with distilled water. The RGO was then re-suspended in 0.1 wt% SDS (sodium dodecyl benzene sulphonate) aq. solution. Diazonium salt of 4-aminothiophenol (4-ATP) was prepared by mixing 70 mg 4-ATP with 200 mg $NaNO_2$ in 40 mL distilled water at 0-5°C followed by the addition of 3 mL 6 M HCl solution (ice cold) slowly to the above mixture. A gradual change of the solution color to pale yellow indicated the formation of diazonium salt. The mixture was then slowly (and with constant stirring) added to the RGO suspension (at 0-5°C) and allowed to stir for another 4 h. Subsequently, the reaction mixture was filtered, washed with DI water and resuspended in DMF to remove the excess SDS surfactant. The suspension was finally filtered and washed to get –Ph-SH functionalized RGO (RGO-SH).

For the synthesis of CdSe QDs, 18 mg of CdO was taken in a four-neck RB flask along with 0.6 ml oleic acid and 10 ml 1-octadecene (ODE). A Se-precursor (Se-TOP) was prepared by dissolving 32 mg Se powder in 5 ml ODE containing 0.6 mL trioctylphosphine (TOP) by slight warming at 60°C. The RB containing CdO was then heated at 190°C when brown colored CdO dissolved to give a colorless solution (Cd-oleate). The heating was continued until it reached to 230°C, when 1 ml Se-TOP was quickly injected into the reaction mixture when the solution turned light yellow due to the formation of very small CdSe QDs. The heating was subsequently stopped and the particles were allowed to settle at that temperature. Aliquotes were collected at different time interval (30 sec, 1 min, 3 min, 5 min, and 10 min) to get different particle sizes. The nanoparticles (NPs) were then precipitated out from the solution by using small amount of hexane followed by copious amount of ethanol. These were then centrifuged and washed. This procedure was repeated 5-6 times to get pure nanocrystals. The precipitate was then vacuum dried to obtain dry powder of CdSe nanoparticles. So prepared particles have narrow size distribution. These prepared oleic acid capped CdSe NPs (CdSe-OA) was then exchanged by simply mixing the DMF suspension of RGO-SH with toluene soluble CdSe-OA with little amount of ethanol to enhance the miscibility of the two solvents. The hybrid was then obtained by centrifugation at 3000 rpm for 5 min followed by repeated washing with toluene and ethanol.

Powder X-ray Diffraction patterns were recorded on a Phillips PANalytical diffractometr with CuKα radiation ($\lambda = 1.5406$ Å), with a scan speed of 2° min^{-1} and a step size of 0.02° in 2θ. For measurements, samples were coated directly on XRD plates. FTIR spectra were taken on a PERKIN ELMER FT-IR SPECTRUM (Nicolet) spectrometer. All Raman spectroscopy measurements were carried out at room temperature on an HR 800 Raman spectrophotometer (Jobin Yvon HORIBA, France) using monochromatic radiation emitted by a Ar^+ laser (514 nm), operating at 20 mW. The experiment was repeated several times to verify the consistency of the spectra. Transmission Electron microscopy was carried out by a JEOL JEM 1200 EX operated at an accelerating voltage of 200 kV with a resolution of not less than 3-4 nm. UV-VIS spectra were recorded using Carry Win 50 (Agilent Tech.) after dispersing the materials in toluene (for CdSe NPs) and in dimethylformamide (DMF) (for Graphene-SH). Steady-state photoluminescenc emission was carried out using a Fluorolog HORIBA Jobin Yvon fluorescence spectrophotometer. EDAX analysis was performed using a Quanta FEI 200-3D scanning electron microscope (SEM) equipped with Phoenix energy dispersive analysis of X-ray (EDX). Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm^{-1} region or using a Diamond ATR (Golden Gate). All contact angle measurements were performed on a GBX model (DIGIDROP contact angle instrument) using Windrop software. The sessile contact angle measurements were performed after making thin film of the materials on FTO coated glass by electrophoretic deposition technique. Extreme care has been taken in carrying out these measurements to monitor contact angle values within 1-2 minutes to avoid the evaporation effects. All contact angle measurements were carried out at room temperature (27 °C) and constant humidity (40-50%) with a standard deviation of ± 2°. Photoconductivity of the sample was measured by two probe method using KEITHLEY source meter and voltmeter in presence of 80 W tungsten lamp.

Section S2 FTIR Analysis of CdSe QDs

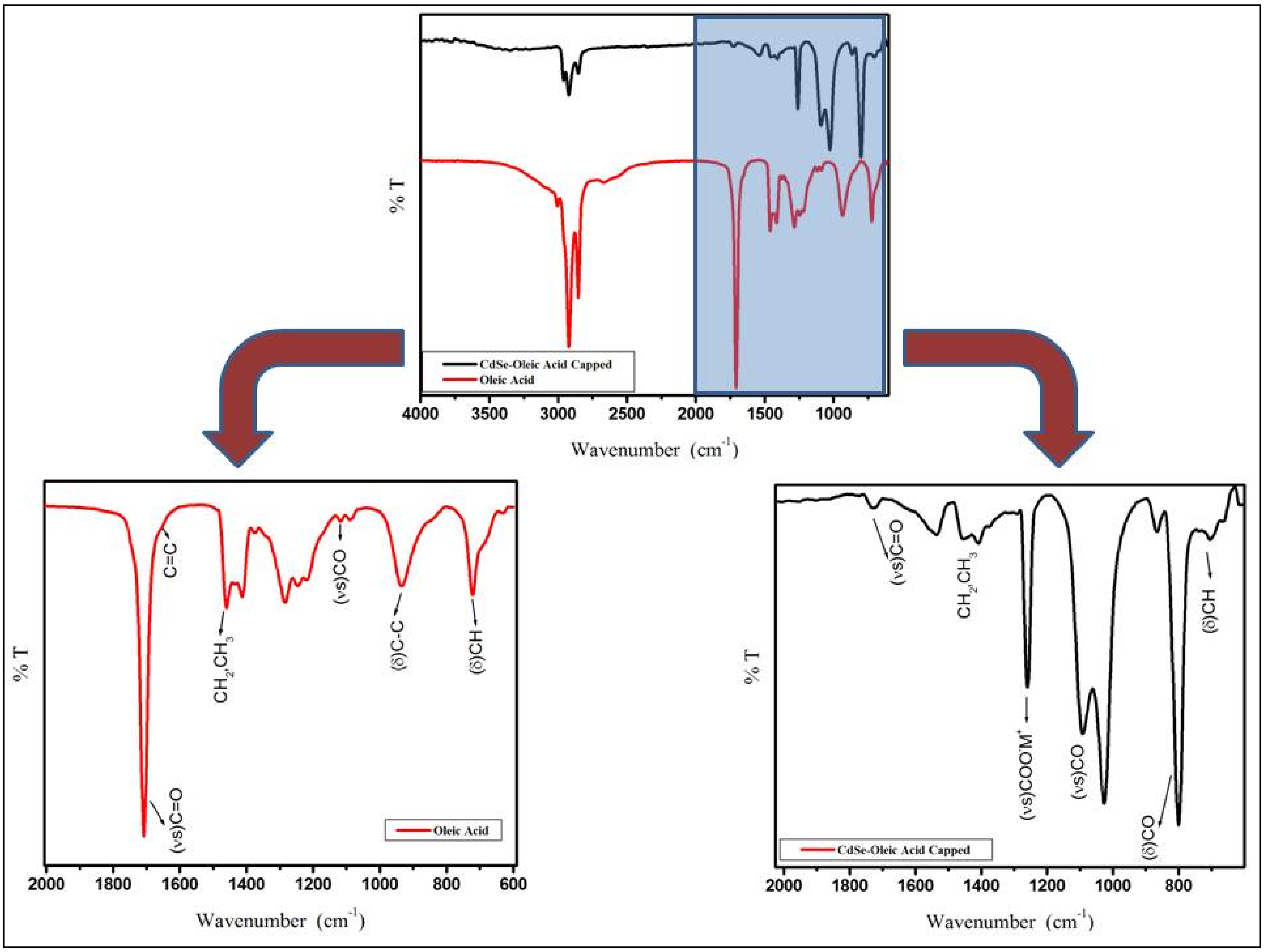

Figure S1: ATR-FTIR spectra of (a) pure oleic acid and (b) CdSe QDs capped by oleic acid. Two Spectra indicate binding of oleic acid on CdSe surface.

Section S3 EDAX Analysis

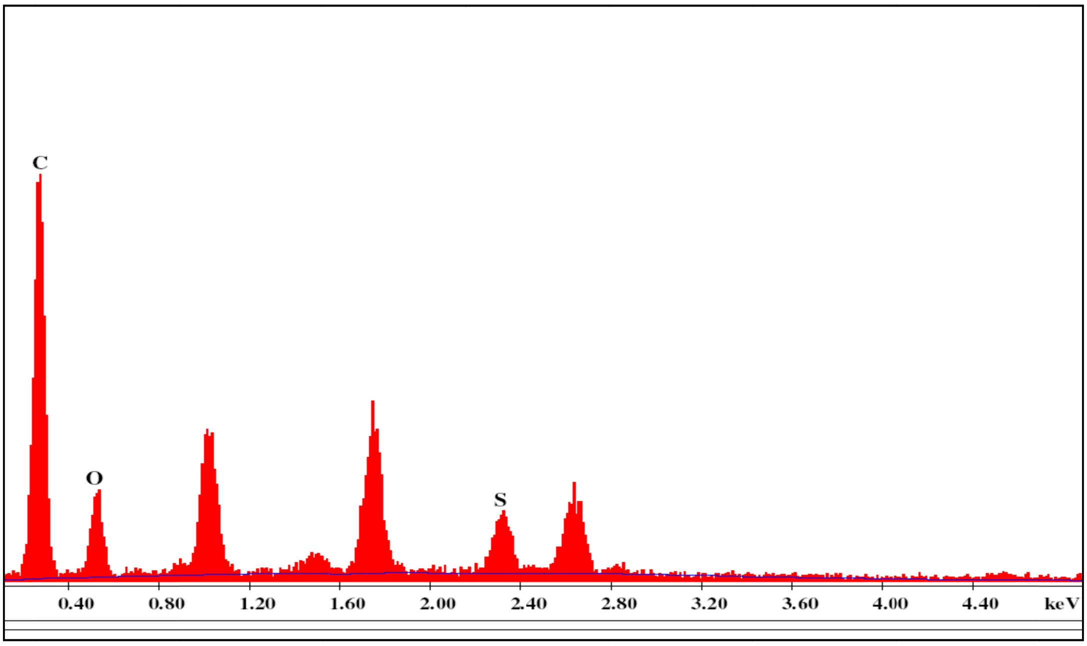

Figure S2**:** Elemental analysis of thiol (-SH) functionalized graphene.

Section S4 Cyclic Voltammetry Analysis

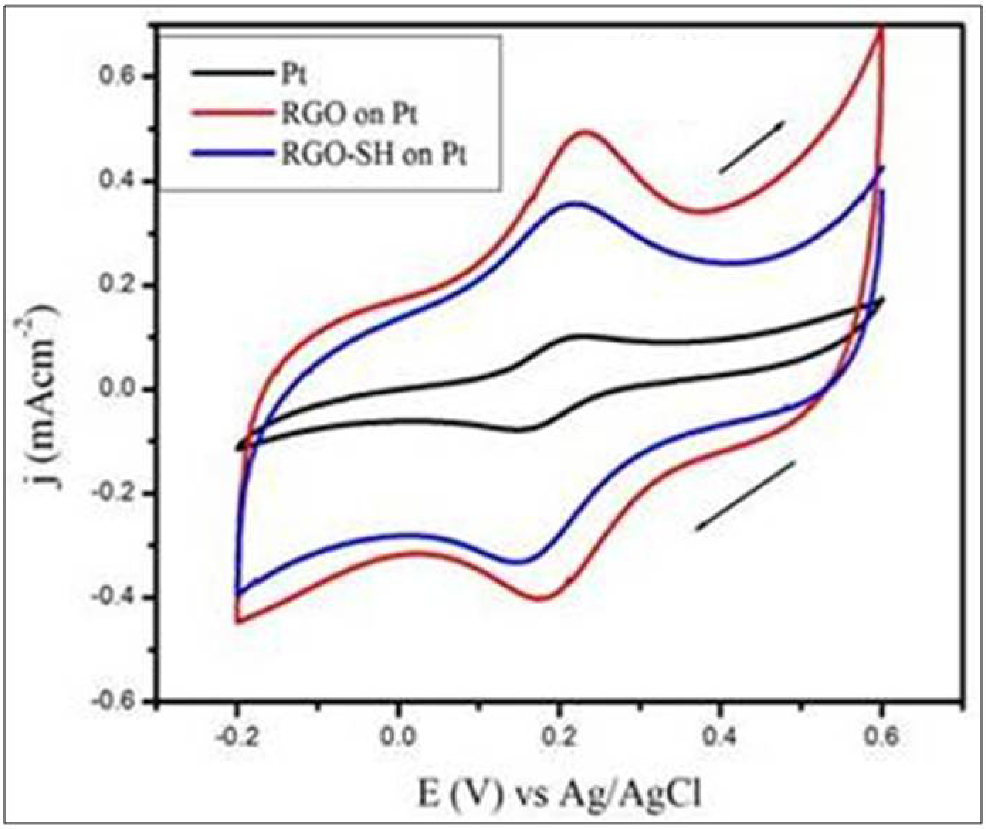

Figure S3: Cyclic voltammogram of RGO coated on Pt electrode (2 mm dia) in 0.5 mM ferrocene methanol containing 0.1 M KCl aqueous solution; Ag/AgCl was used as reference electrode and Pt-foil as counter electrode. Scan rate was 10 mVs^{-1}. For comparison CV of Pt disk also has been shown.

Section S5 Impedance Analysis

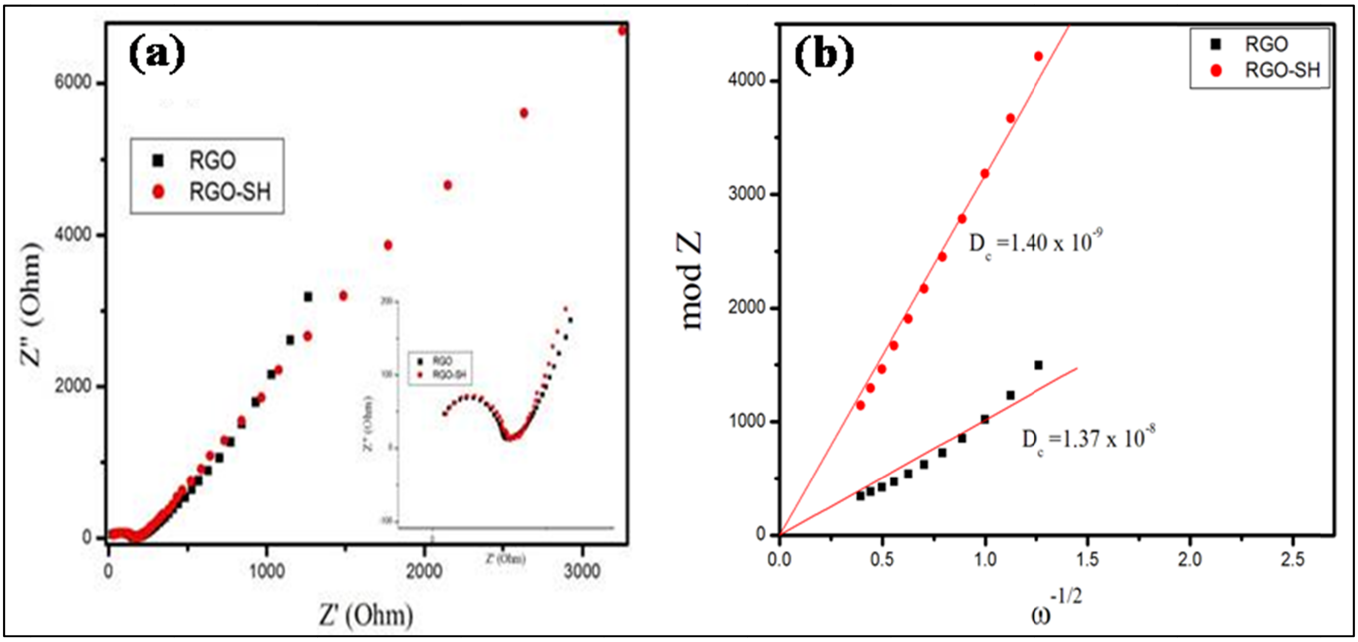

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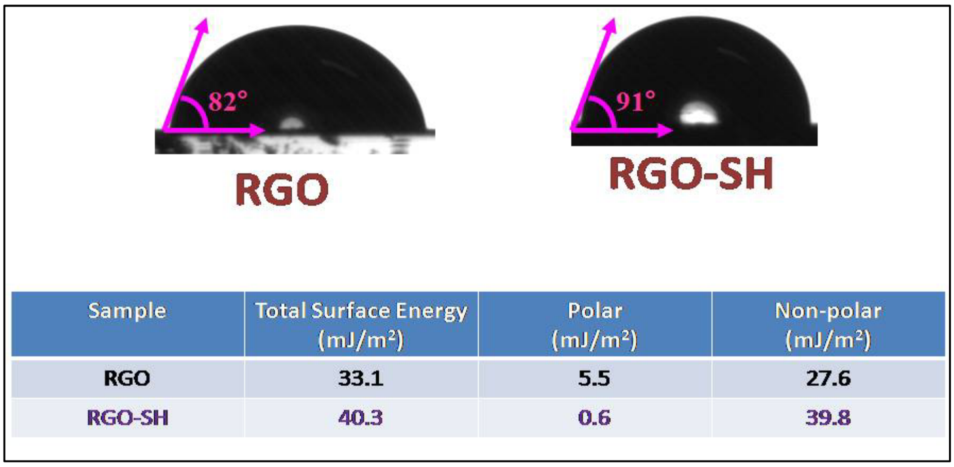
Figure S4: (a) Nyquist plot for the same system before and after –SH functionalization. The R_{ct} increases after functionalization. (c) $\omega^{-1/2}$ vs mod. Z plot from the low frequency part of the Nyquist plot for the calculation of diffusion coefficient of the ferrocene methanol.

Section S6 Contact Angle Measurement



Sample	Total Surface Energy (mJ/m²)	Polar (mJ/m²)	Non-polar (mJ/m²)
RGO	33.1	5.5	27.6
RGO-SH	40.3	0.6	39.8

***Figure S5*:** Water contact angle on RGO and RGO-SH surface. The film of each sample was made by electrophoretic deposition (solvent N-methyl pyrrolidone for RGO and Dimethylformamide for RGO-SH) on clean FTO plates and dried at 100°C under vacuum to get smooth surface so as to minimize errors due to surface roughness.

Section S7 UV-VIS Analysis

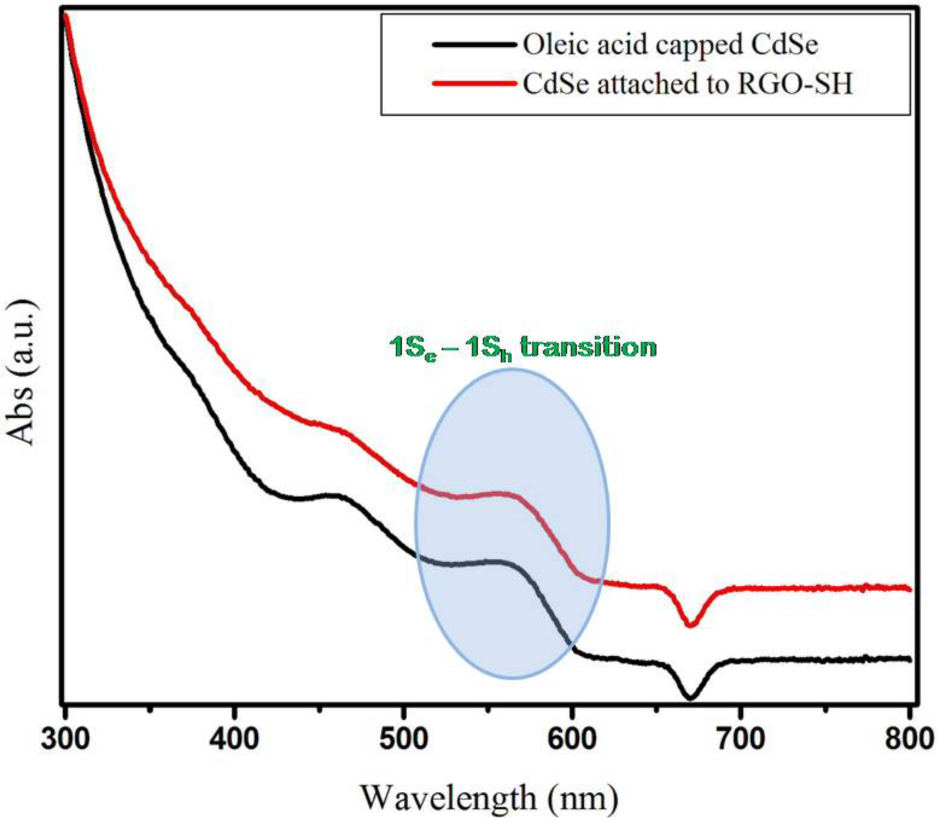


Figure S6: UV-VIS absorbance plot of oleic acid capped (blue line) CdSe QD (4.9 nm) in toluene and CdSe-RGO-SH composite (red line) in toluene-DMF-ethanol mixture.

Section S8 Photoluminescence study

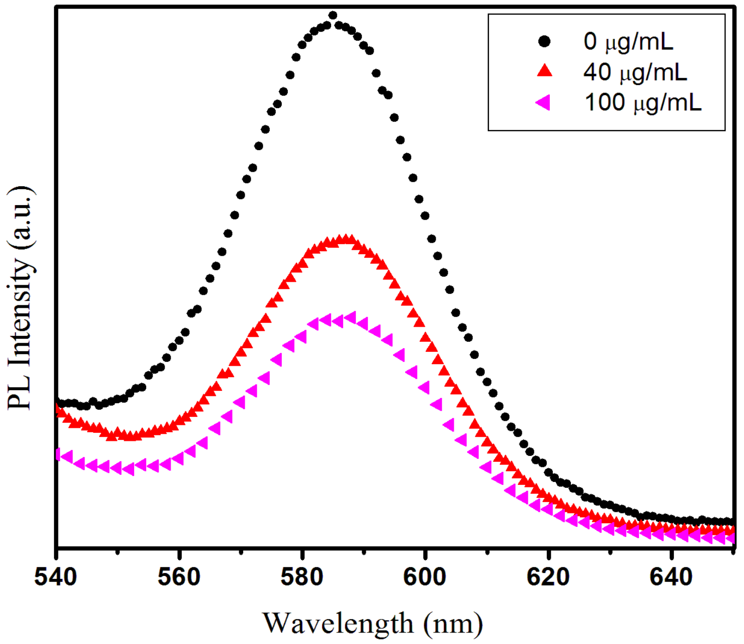


Figure S7: Photoluminescence quenching of RGO-SH-CdSe (4.9 nm) composite showing enhanced quenching with the increase in RGO-SH amount. Inset shows the amount of RGO-SH added.

Section S8 Powder X-ray Diffraction

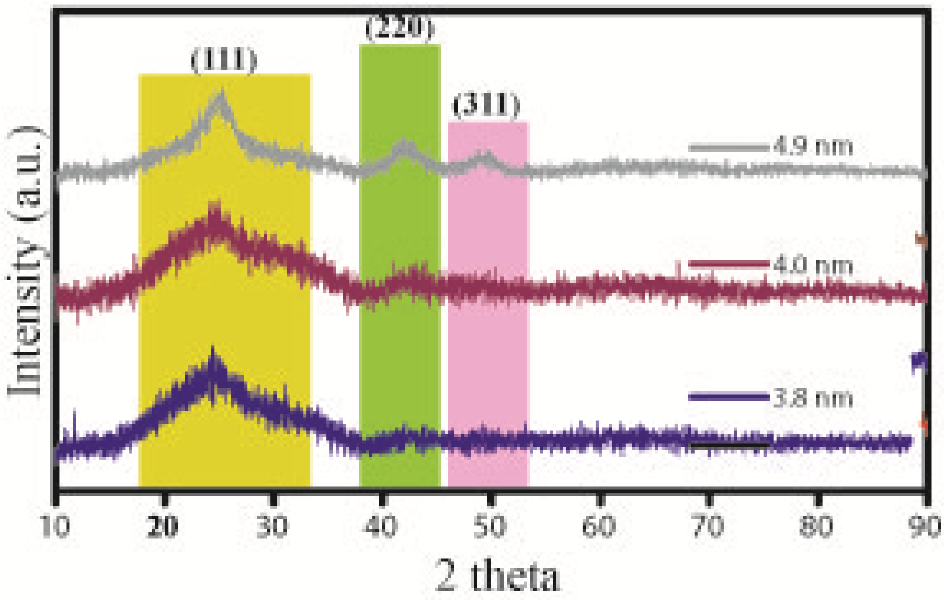


***Figure S9*: Representative powder X-ray diffraction pattern of oleic acid capped CdSe nanoparticles showing crystalline nature and cubic phase formation.**

Figure S9 shows the X-ray diffraction patterns of oleic acid capped CdSe nanoparticles. The diffractogram confirms the crystallinity of the CdSe nanoparticles. Three main diffraction peaks could be identified in the pattern and those peaks match well with the reflections from (111), (220) and (311) planes indicating cubic phase formation (zinc blende phase, JCPDS card no.19-0191).

Section S9 TEM

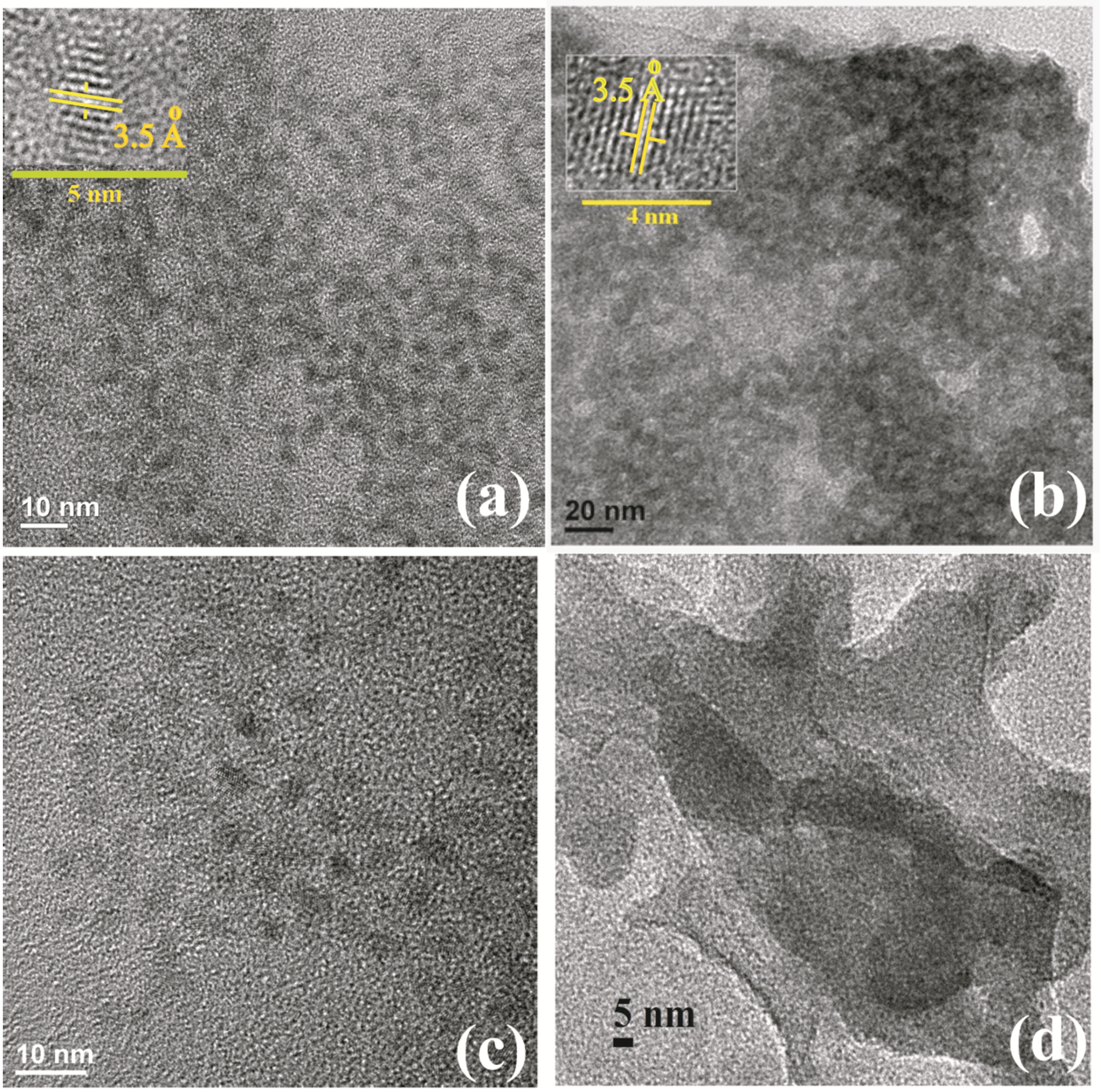


Figure S10: High resolution TEM images of (a) Oleic acid capped CdSe QDs (4 nm) before ligand exchange, (b) RGO-SH-CdSe QDs (4 nm) hybrid after ligand exchange, (c) Oleic acid capped CdSe QDs (4.9 nm) before ligand exchange, (d) CdSe QDs physically adsorbed on graphene (RGO).

Fig. S10 shows high resolution TEM images of CdSe QDs (size 4 and 4.9 nm) (fig. (a) and (c)) and their hybrids with RGO-SH (thiolated graphene) (fig. (b). Fig. S10 (d) represents CdSe QDs physically adsorbed on graphene surface. Size of QDs remains invariant before and after ligand exchange with thiolated graphene as has been observed in TEM images (fig. (a) and (b)). It is also clear from fig. (a) and (b) that the basic crystal structure (cubic phase) does not change on ligand exchange because the d-spacing (3.5 Å) is found to be constant before and after ligand exchange. Thus it proves our method of

CdSe decoration on RGO-SH to be an efficient one. Fig. (d) also suggests that the physical attachment of QDs on graphene does not provide good control for making such hybrid heterostructures.

Section S10 Photoconductivity measurement

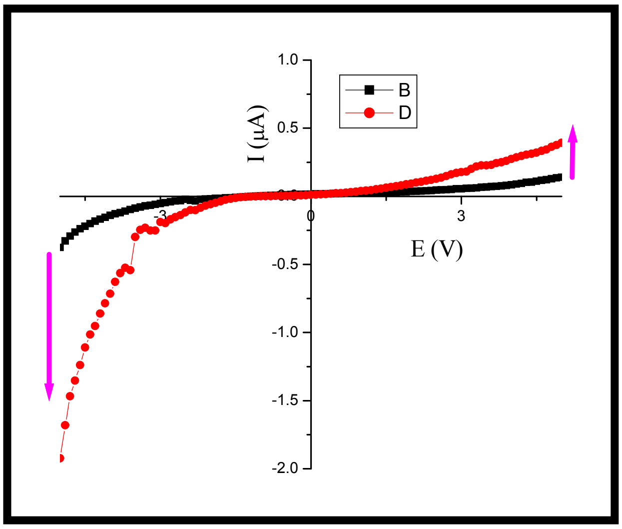


Figure S11**:** I-V characteristic of the composite CdSe-RGO-SH. The current increases significantly on irradiation with ambient light. Samples were drop-casted on gold channels 2.5 µm wide apart. These electrodes were purchased from Fraunhofer institute in Germany. All measurements were carried out at atmospheric conditions using Agilent 4156 C semiconductor parameter analyser and Semiprobe probe station.

Section S11 Additional Raman Study

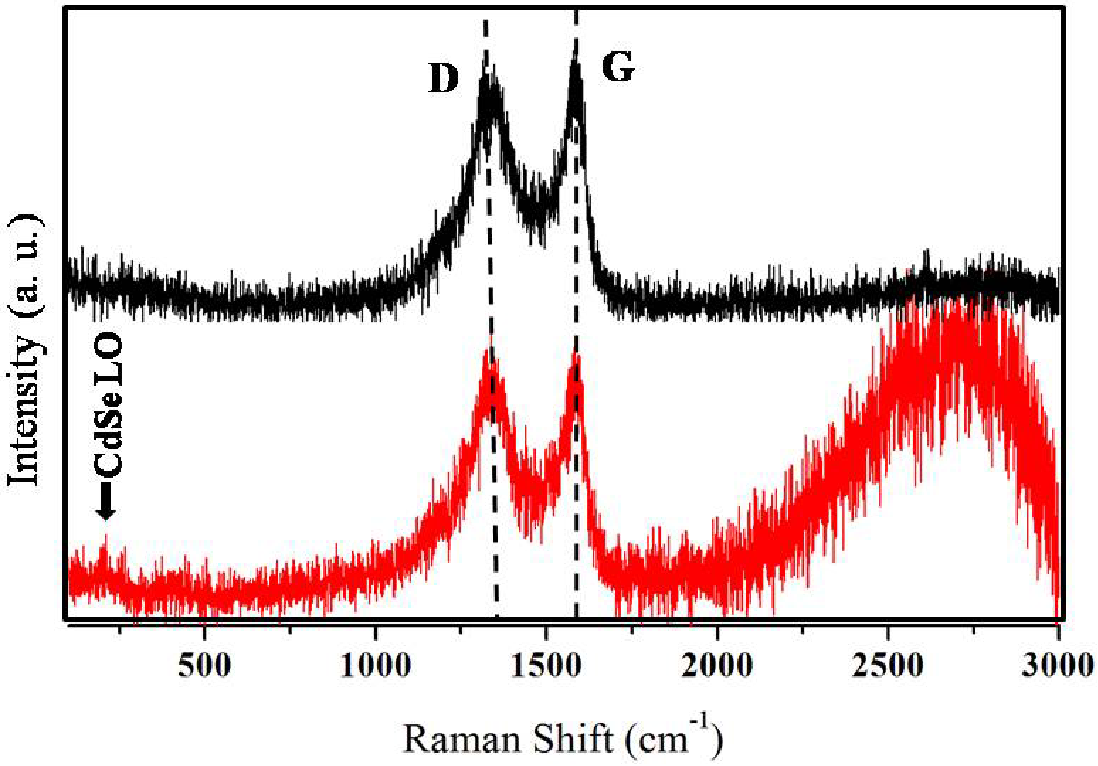


Figure S12: Raman spectra of CdSe QDs (4.9 nm)-pristine graphene hybrid. CdSe (4.9 nm) was drop casted on pristine graphene (without thiol group) and the pristine graphene was previously coated on fresh, cleaned Si-wafer.

Fig. S12 is the representative Raman spectra of the physical mixture of CdSe QD (size 4.9 nm)-pristine graphene, i.e., graphene surface is free from any thiol group unlike the thiolated graphene used for our study. D- and G- bands of graphene are clearly seen both in case of pristine graphene (without QDs) as well as in case of the physical mixture of QDs-pristine graphene. It is clear from the plot that there is no shift of D or G-band after putting CdSe QDs on pristine graphene unlike the case for thiolated graphene-CdSe QDs hybrids, where ~13 cm^{-1} red shift was observed on attaching CdSe QDs. The shift is attributed to the electron transfer from excited state CdSe QD to thiolated graphene surface. Absence of such shift in case of pristine graphene and CdSe physical mixture thus indicates that the thiolated graphene is more efficient in charge transfer than the pristine graphene.