Electronic Supplementary Information

Ultrafast carrier dynamics in 2D-2D Hybrid Structures of Functionalized GO and CdSe Nanoplatelets

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Synthesis of Graphene Oxide (GO)

The uses of Hummer's method to prepare GO eliminates the need for metal catalysts in contrast to techniques such as chemical vapour deposition. The presence of metallic catalysts in carbonaceous nanomaterials used in synthesis can induce cytotoxicity [1]. Here, we use modified Hummers [2] method to prepare GO. Briefly, A mixture of graphite powder (3 g), $NaNO_3$ (1.5 g) and cold H_2SO_4 (50 mL) was cooled down to 0°C. Then, $KMnO_4$ (9 g) was added slowly, keeping the temperature below 5°C. The mixture was then stirred at room temperature for half an hour. Small amount of water was added just to dissolve the slurry and the temperature was increased to 90°C, kept there for overnight. The mixture was cooled down and diluted with 300 mL of water. 30 mL of 30% H_2O_2 solution was treated until the effervescence was ceased. The solution was left for overnight and then the brown precipitate was centrifuged with 10% HCl solution for several times, finally with water. The product was sonicated with water to disperse and then large particles were centrifuged out at 3000 rpm. The desired particles were centrifuged at 12000 rpm, collected and dried at vacuum.

Surface functionalized graphene oxide

Fourier transform infrared (FTIR) spectra of GO, rGO-OAm and G-Ph-SH samples are shown in fig. S1A. The appearance of asymmetric bands at $\sim$ 2849 cm^{-1} and $\sim$ 2919 cm^{-1} are due to the C-H stretching vibrations after the amine modification (Fig. S1A-b,ESI†). The bands at $\sim$ 1550 cm^{-1} and $\sim$ 1430 cm^{-1} are for N-H bending and C–N stretching frequencies, respectively due to the presence of amine group. The FTIR spectra clearly suggest that the amine molecules are covalently attached to the graphene oxide through chemical modification. The band at $\sim$ 1640 cm^{-1} in the all the spectra is assigned to the carbonyl

stretching vibration, which further confirms the formation of an amide bond between the graphene oxide and the amine molecules (Fig. S1A). Similarly, UV-visible spectra of all modified composites of GO suggest the surface modification (Fig. S1B,ESI†). The GO spectrum shows a characteristic absorption peak at 235 nm corresponding to the $\pi \rightarrow \pi^*$ transition of aromatic C=C bond. After functionalization, the red shifted peaks are at ~ 278 nm and 289 nm, (Fig. S1B) suggesting the restoration of electronic conjugation within the GO sheets.[3]
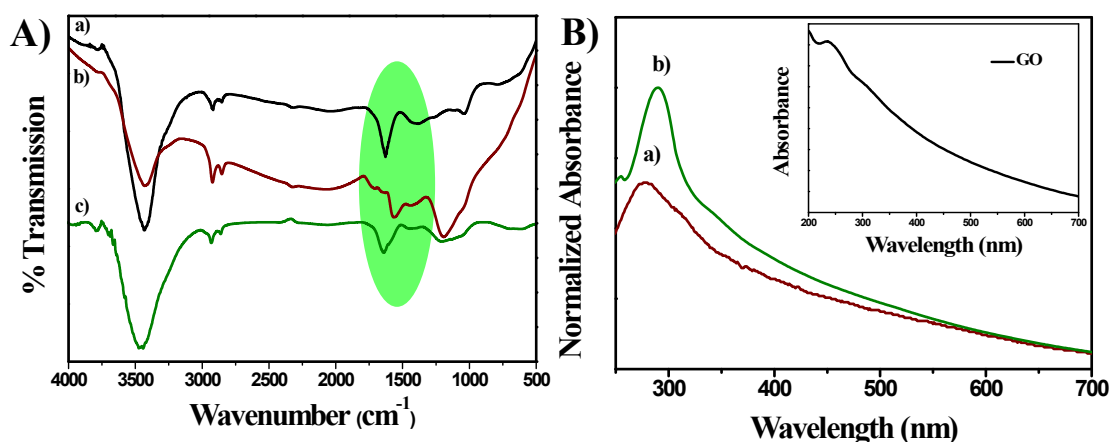

Fig. S1 (A) FTIR spectra of a) GO, b) rGO-OAm, and c) G-Ph-SH, respectively, (B) UV-visible spectra of GO (inset), a) rGO-OAm, and b) G-Ph-SH, respectively.

Raman spectroscopy is most powerful characterization technique to understand the electronic interaction within GO sheets after surface modification. All the measurements were carried out at 532 nm excitation. The Raman spectra of the all the functionalized material consist of characteristic graphene oxide peaks, as well as peaks corresponding to respective functionalized groups (Fig. S2). GO shows two characteristic D and G bands at 1356 and 1595 cm^{-1} with an intensity ratio (I_D/I_G) of 0.87 (Fig. S2A-a). The D and G bands of the functionalized material are found to be at ~ 1341 cm^{-1}, 1349 cm^{-1} and 1595 cm^{-1} and 1594 cm^{-1} (Fig. S2A, b-c), respectively. The intensity ratio of 'D' and 'G' bands (I_D/I_G) are found to be 0.97 and 0.99, respectively which signifies that the amount of defects state before and after thiol functionalization which remains almost same.[4] Both the functionalized GO show strong band at ~ 1430 cm^{-1} for C–N anti symmetrical stretching and ~ 1130 cm^{-1} band for C–H in plane deformation and ring stretching (S2. 1A b-c).[5] The shifting of the bands and the appearance of characteristic amide bands reveal that GO is successfully modified by long chain oleylamine (OAm) and 4-aminothiophenol (4-ATP). Figure S3 shows the SEM image of as synthesized functionalized reduced graphene oxide. Elemental mapping analysis confirms the oleylamine functionalization of GO (Fig. S2B). The presence of carbon,

nitrogen, oxygen and sulphur are found in the -SH functionalized graphene oxide, G-Ph-SH (Fig. S3A). These findings suggest that thiol group (-SH) is attached on the surface of rGO-OAm. Fig. S3C shows the digital photographs of G-Ph-SH in different organic solvents (DMF, toluene) which indicate that the -SH functionalized rGO would be well dispersed in non-polar solvent. The surface modification reduces the hydrophilic character of graphene oxide sheets by forming amide bonds to the carboxyl groups of graphite oxide.
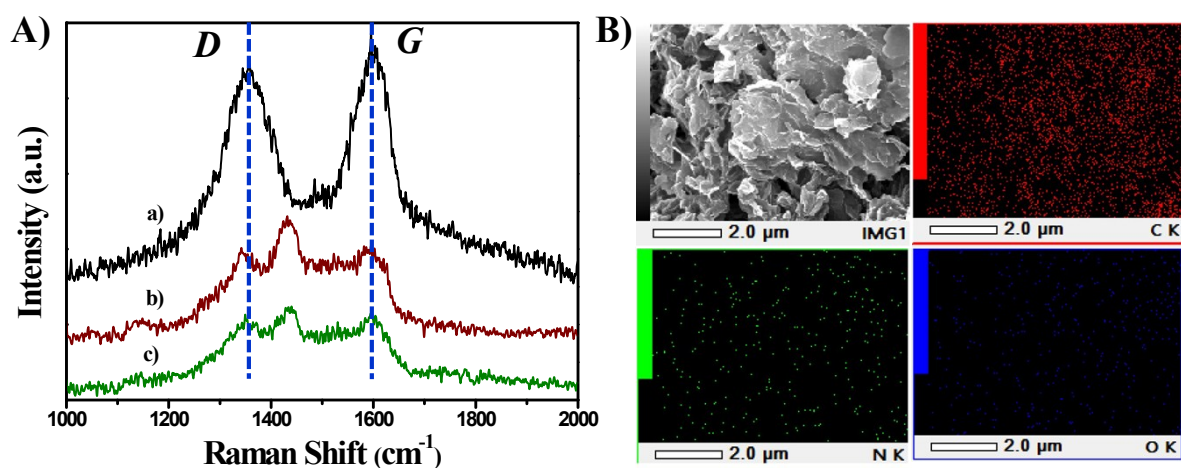

Fig. S2 (A) Raman spectra of a) GO, b) rGO-OAm, and c) G-Ph-SH, respectively, (B) SEM image and EDS elemental mapping for the oleylamine functionalized GO (rGO-OAm).
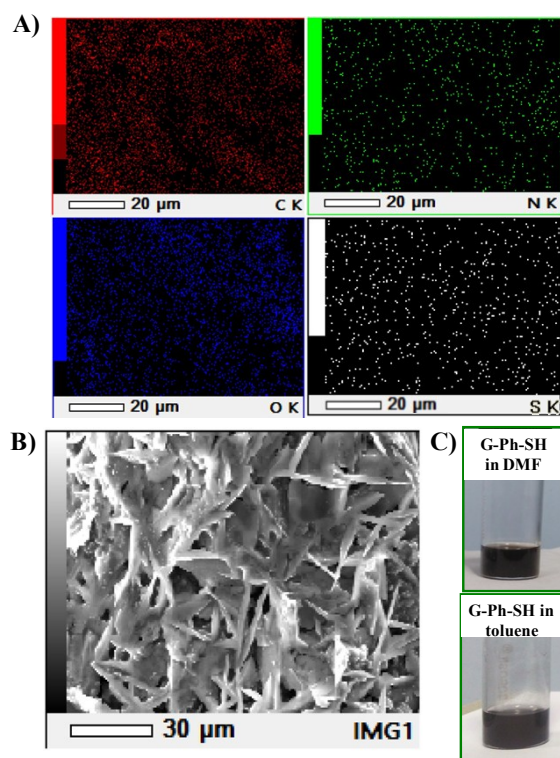
Fig. S3 (A) Elemental (carbon, nitrogen, oxygen and sulphur) mapping in of G-Ph-SH, (B) SEM image of G-Ph-SH, (C) Digital photographs of solubility of G-Ph-SH in different organic solvents (DMF, toluene).

The XPS technique is used to evaluate the functionalization on the surface of graphene oxide.[6] Fig. S4 shows the C 1s, O 1s, N 1s core-level X-ray photoelectron spectra (XPS) of rGO-OAm. The C 1s peak is de-convoluted into three components (Fig. S4a). The most intense peak at 284.5 eV is due to sp^2 C-C bonds of graphitic carbon. The components at 285.4 eV is often assigned to sp^3 C-C/C-N. The peak for more –oxidised component, C-O at 287.6, is not present significantly. The broad O 1s core-level spectrum suggests the presence of more than one O-containing species (Fig. S4b). The peak at 531 eV corresponds to O=C surface groups and the second peak at 531.9 eV is associated with O-C bonds, indicating the existence of functional groups on the graphene surface. More information on the functionalization is obtained by looking at the N 1s core level. As illustrated in Fig. S4C , the N 1s spectrum of sample is fitted to two components at 399.4 eV and 400.5 eV, respectively. These findings suggest that amidation occurs between GO and primary amine proceeds via condensation. The successful thiol functionalization is further confirmed by the core-level spectrum of S 2p (Fig. S4d) which is de-convoluted into several peaks including

H-S-C (~ 163.6 eV), R-S-C (~164.8 eV), and S-O (~168 eV). Results are in good agreement with the covalent attachment of phenylsulfenyl moiety towards rGO.[6] The reduction is also observed from the C 1s, O 1s and N 1s and core-level spectra as shown in Fig. S4 (a-c).
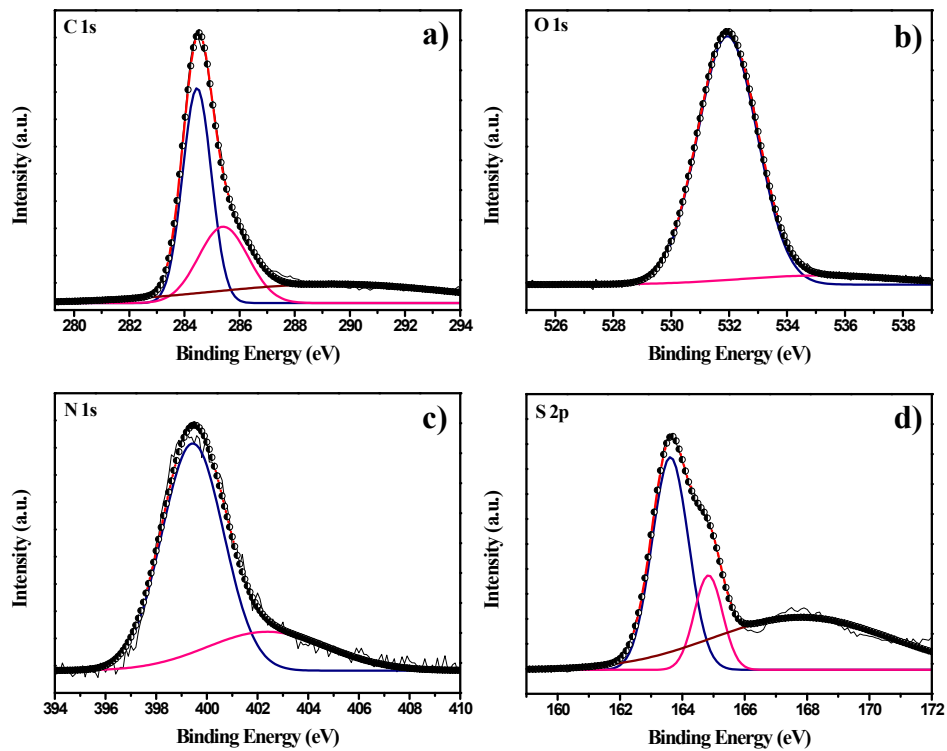

Fig.S4 XPS spectra of a) C 1s, b) O 1s, c) N 1s and d) S 2p for G-Ph-SH nanosheet.
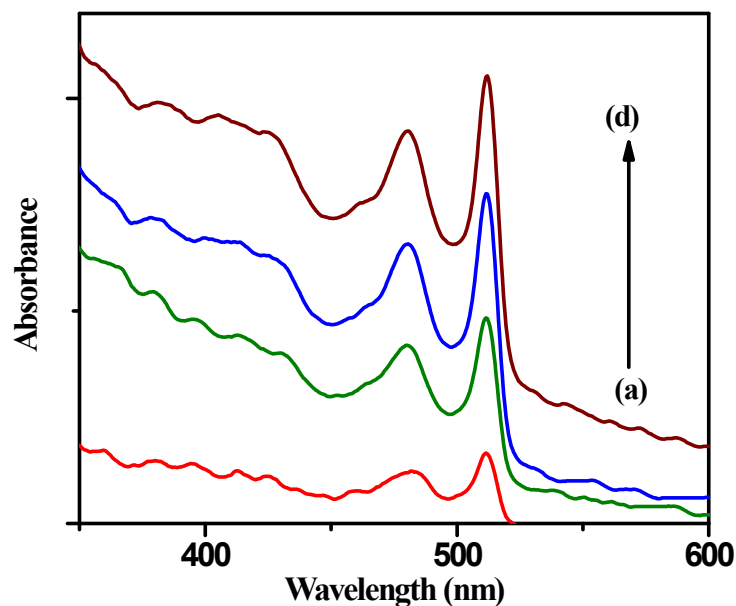
Fig. S5 UV-Vis spectra of pure CdSe NPLs, and composite with gradual increase of G-Ph-SH up to 100μg (a-d).

Stern-Volmer Calculation:

We studied the fluorescence quenching of CdSe NPLs with changing the quencher (GO) concentration. A gradual quenching of the fluorescence intensity of CdSe NPLs with increasing concentration of GO is seen in figure below. On the basis of the relationship between quenching of fluorescence intensity and quencher concentration, the Stern-Volmer equation is given by 1

$$F_0/F = 1+ K_q \tau_0 [Q] \qquad\qquad (1)$$

Here, F_0 and F are the relative fluorescence intensity in absence and presence of quencher, respectively. Kq is the bimolecular quenching rate constant; τ_0 is the average lifetime of the CdSe NPLs in the absence of quencher, and [Q] is the concentration of the quencher. Figure S6 shows the Stern-Volmer plots of F_0/F versus [GO]. Linear fitting of the data reveals the dynamic quenching process. Where, 'τ' is the lifetime of CdSe NPLs in presence of quencher. Figure S7 shows the Stern-Volmer plots of τ_0/τ versus [GO]. In this case the Stern-Volmer plots are linear for both intensities and lifetimes, and $F_0/F =\tau_0/\tau$. Hence, quenching of CdSe NPLs is dynamic. Here, we have used up to 100 μg concentration of GO which is used in the present study. Static quenching may occur in higher concentration of quencher.
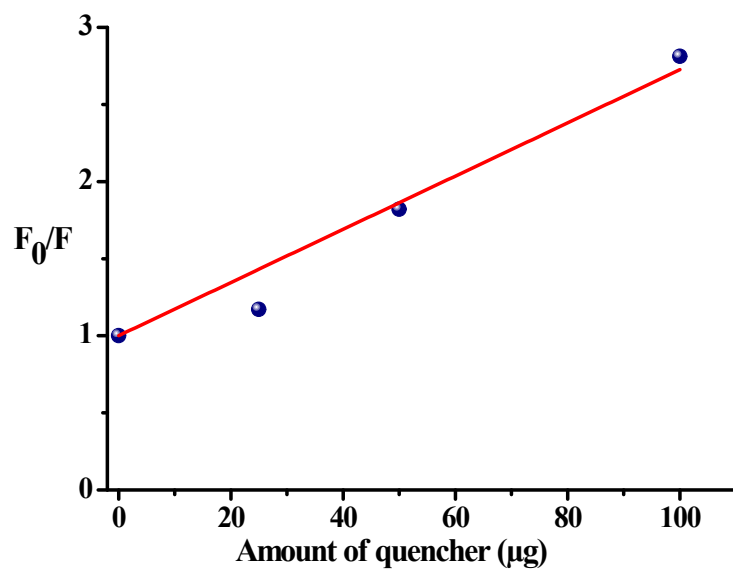
Fig. S6 (A) Stern-Volmer (F_0/F vs [GO]) plot of CdSe NPLs with changing the concentration of G-Ph-SH (0 to 100 µg).
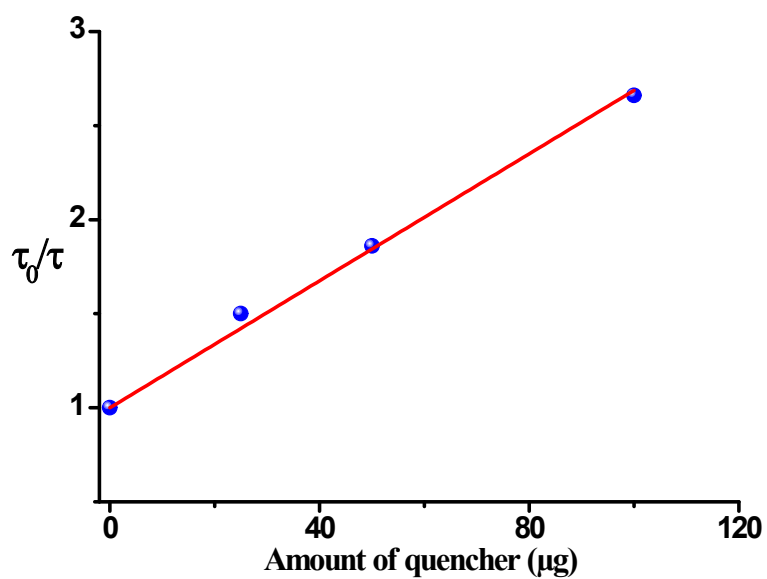

Fig. S7 Stern-Volmer Plot (τ_0/τ vs [GO]) of CdSe NPLs with changing the concentration of G-Ph-SH (0 to 100 µg).

References

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