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SUPPLEMENTARY INFORMATION

Resonant energy transfer in van der Waal heterostacked MoS_2 - functionalized graphene quantum dots composite with *ab-initio* validation

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Experimental Procedure

a. Preparation of exfoliated MoS_2 nanosheets:

To exfoliate the bulk MoS_2 powder into single or few layered MoS_2 nanosheets, we used various kind of pure and mixed solvents like pure methanol, mixture of methanol-water (1:1 ratio), pure isopropanol and mixture of isopropanol -water (1:1 ratio) to disperse the bulk MoS_2 powder. However, we observed that pure isopropanol provided the best yield and for better dispersion and exfoliation of MoS_2. Additionally, J. N. Coleman [1] *et al*. also reported to exfoliate layered MoS_2 with the standard concentration of 7.5 mg/ml loading with sonication power 285W, sonication time 60 mins, centrifuge rpm 1500 and centrifuge time 45 minutes for optimal optical characterizations as a starting reference.

It was also reported that the liquid exfoliation of MoS_2 by probe sonication procedure at nominal to medium power output of ~ 285 - 400W with slightly higher centrifugation speed between ~1500 – 3000 rpm also yields better exfoliation for obtaining few layered flakes. [2,3] Taking these into

considerations, we have changed a few experimental parameters for the controlled synthesis of few layered MoS_2 nanosheets and the final sample was prepared as mentioned below.

a. Optimised MoS_2 sheet liquid exfoliation

Few-layered MoS_2 nanosheets were exfoliated from bulk MoS_2 powder (<2 μm particle size) as obtained from by dispersing in iso-propanol solution (IPA) with standard loading of 1 mg/ml, followed by horn sonication for 1h at 285W power. Finally, the product was centrifuged for 1h at 1500 rpm to obtain a stable dispersion and separate the bulk before further characterizations. [1]

b. Preparation of amino-functionalized graphene quantum dots (GQDs):

At first, the graphene oxide (GO) was synthesized from graphite powder by following the Hummers' method. [4] The amine functionalized GQDs were further synthesized from GO solution by hydrothermal process. For the synthesis of GQDs, 10 ml of GO solution (1 mg/1 ml loading), 10 ml of de-ionized water and 6 ml of ammonia (30% by wt.) solution was added together in a beaker and continuously stirred for 25 - 30 minutes. The resultant mixture was transferred into Teflon - lined autoclave (50 mL) and heated at 150 °C in a hot oven for 6 h. The solution was naturally brought down to room temperature and subsequently large fragments retained within the suspension were filtered out by using a 0.02μm anopore inorganic membrane (Anodisc TM, Whatman). The GQDs were present in the supernatant (filtrate). The resultant transparent supernatant was heated at ~ 90 ºC for 1 h to vaporize the excess ammonia present with in the GQDs solution. The final transparent solution consisting of amine functionalized GQDs was collected and used for further experiments and characterization. [5,6]

c. Preparation of MoS_2 – GQD composition:

In a typical synthesis procedure, as-prepared GQD solution was mixed with exfoliated MoS_2 nanosheets with (1:1) volumetric loading and mildly stirred for 10 minutes at ambient conditions. Finally, the solution was collected and kept aside for further characterizations.

For the preparation of MoS_2 – amino functionalized GQDs composite variation, various loading ratios are maintained following the same mixing procedure as mentioned above. The volume ratio of the

MoS_2 and GQD were maintained as 1:1 (5ml MoS_2 – 5 ml GQD) and 1:3 (5 ml MoS_2 – 15 ml GQD) loading for the synthesis of MoS_2 – GQD composite.

Characterizations

All samples were characterized by field emission scanning electron microscope (FESEM, Hitachi, S-4800), high resolution transmission electron microscopy (HRTEM, JEOL-JEM 2010,200 KV), dynamic light scattering (DLS) measuring system, Fourier transformed infrared spectrophotometer (FTIR-8400S), Raman/AFM spectrometer (Witec Alpha300R, λ_{ex}=532 nm) for structural morphological and compositional analysis. Optical band gap was determined by UV–Vis spectrophotometer (Shimadzu UV-3600). The steady state photoluminescence measurements were conducted using a JASCO fluorescence spectrometer with Xenon flash lamp excitation source. All photoluminescence data was analyzed after solvent corrected background subtraction. The time resolved photoluminescence decay measurements were performed by Edinburgh FLS980 spectrometer with the help of time-correlated single-photon counting (TCSPC) apparatus using a 350 nm excitation with picosecond diode laser.

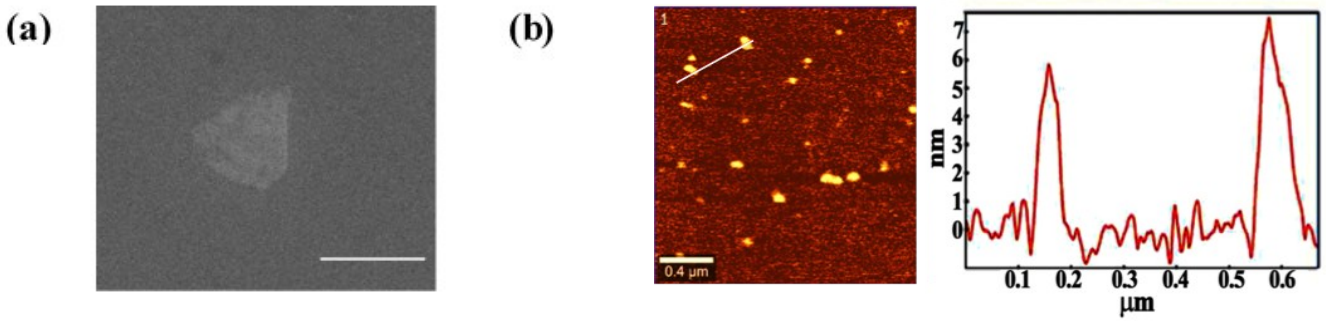

Figure S1: (a) FESEM image of as-exfoliated MoS_2 Sheet. Scalebar 400 nm (b) AFM topography and height profile of the optimized liquid exfoliated MoS_2 nanosheet sample taken along the white line

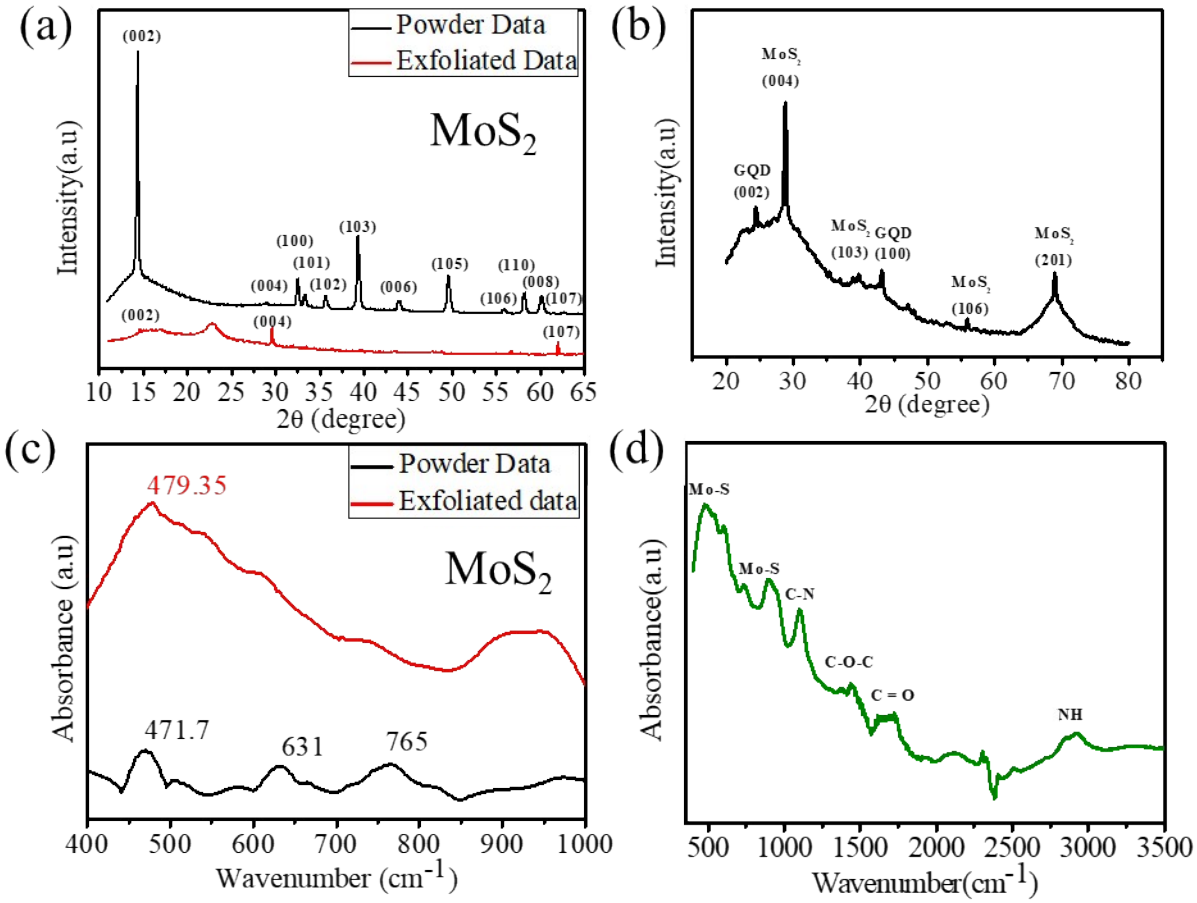

Figure S2: (a) X-Ray diffraction spectra for bulk MoS_2, exfoliated MoS_2 and (b) MoS_2-GQD (c) FTIR spectra for bulk MoS_2, exfoliated MoS_2 and (d) MoS_2 -GQD

The X-Ray diffraction peaks for crystalline MoS_2 nanosheets have been indexed according to JCPDS card no: 771716 as shown in figure S2 (a). Figure S2 (c) shows the FTIR spectra of bulk and exfoliated MoS_2 nanosheets with Mo-S stretching at 471.7cm^{-1} and 479.3 cm^{-1}, oxysulphate stretching at 631 cm^{-1} and Mo-O stretching at 765 cm^{-1} in the bulk form. [7, 8] Figure S2 (d) depicts the FTIR spectrum of the MoS2-GQD material with additional C-N, C-O-C, C=O and a broad in-plane N-H (amino) stretching ~ 2800-3100 cm^{-1} due to addition of amino-functionalized GQD in the system along with the typical Mo-S stretching coming from the MoS_2 nanosheets.

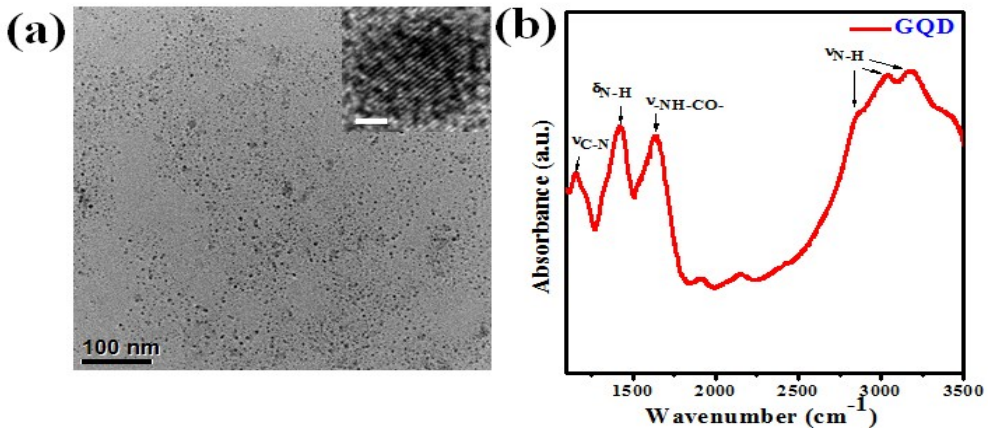

Figure S3: (a) HRTEM

micrograph of the as-synthesized amino- functionalized GQD sample with the upper right inset showing the high magnification lattice image with scalebar 1 nm (b) FTIR spectrum of amino functionalized graphene quantum dot

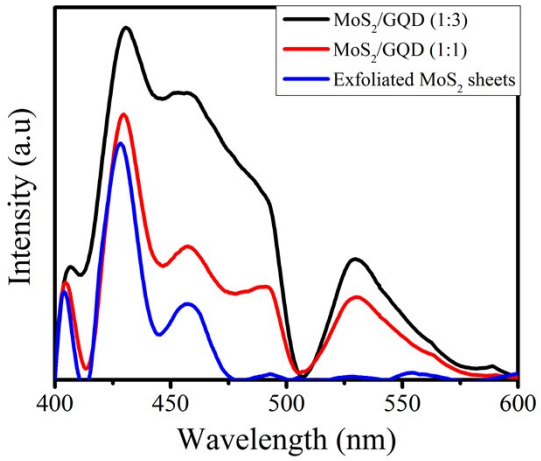

Figure S4: Photoluminescence dependence on Volumetric loading variation of GQD in the heterostructures sample

Computational details and Modeling

We performed first principles calculations using spin polarized Density Functional Theory (DFT) as implemented in the Vienna *ab-initio* Simulation Package (VASP). [9] The Perdew–Burke–Ernzerhof (PBE) functional [10] within the generalized gradient approximation (GGA) was employed to calculate the electronic exchange and correlation terms. The ion cores were described by the projected augmented wave (PAW) method. [11] The present computations involve three different set of atomic models a) a periodic heterostructure of di-vacancy 585 graphene sheet on MoS_2 monolayer, b) a periodic MoS_2 monolayer (ML), bi-layer (BL) and tri-layer configurations (TL) and c) functionalized di-vacancy 585 graphene quantum dot (GQD) on periodic MoS_2 monolayer.

For the periodic heterostructure model(s), plane wave basis up to an energy cut off of 400 eV was utilized. For geometrical optimizations, Brillouin zone integrations were carried out using a k-point grid of 2×2×1 centered at the Γ point and the systems were allowed to fully relax until the forces were converged below 1×10^{-2} eVÅ^{-1} and the total energies were converged below 1×10^{-5} eV per atom. In all computations, a 25Å vacuum slab was deployed along the perpendicular direction to ward off spurious interactions with periodic images. The heterolayer was constructed with a 5×5 graphene layer containing a single 5-8-5 double vacancy defect on top (48 C atoms) and a 4×4 MoS_2 monolayer (16 Mo and 32 S atoms) at the bottom. The initial structure had a negligible ~2.75% lattice mismatch and was then fully relaxed (including both atoms and lattice vectors). The relaxed structure was found to have lattice parameters of 12.439Å × 12.439Å (i.e. intermediate of pristine graphene and MoS_2) and the separation between the two atomic layers was found to be 3.360Å. This relaxed structure was subsequently used in subsequent computations.

For the GQD - periodic MoS_2 model, plane wave basis up to an energy cut off of 450 eV was utilized. The Brillouin zone integrations were carried out within the Monkhorst Pack scheme using 3×3×1 k-points and Γ point for the GQD - periodic MoS_2 heterostructure and the quantum dot system respectively. All the structures were optimized until the total energy converged to less than 10^{-5}eV per atom. In these set of computations, three simple structures were considered to study the interaction between amine functionalized graphene quantum dot and MoS_2: The first structure was the functionalized di-vacancy 585 graphene quantum dot (GQD). The GQD comprised of two units of NH_2 molecule and one $CONH_2$ molecule at the edge. The numbers of C, H, N and O atoms were 53, 21, 3 and 1 respectively. As second structure we considered a 7×7×1 supercell of MoS_2 monolayer which consisted of 49 Mo and 98 S atoms. As the final structure we constructed GQD-MoS_2 heterostructure to mimic the experimentally observed materials by placing the GQD on the 7×7×1 supercell of MoS_2 monolayer, which contained a total of 225 atoms. We considered vacuum of 15 Å along c-axis in these model geometries to avoid spurious interactions.

Ab-initio results

To understand the electronic structure of the composite system further on the PL attributes, we we carried out extensive theoretical *ab-initio* analysis initially by constructing a simple periodic model for vdW graphene – MoS_2 stack. Previous report suggests change of graphene's gapless nature from direct to indirect bandgap takes place when MoS_2 layer is stacked upon it [12] as a result of strain induced in the system due to slight lattice mismatch alignment and subsequent energy minimization. However we have added an additional DV 585 type defect in graphene in order to model chemically prepared graphene samples will always have some structural defects. We optimize the structure and find the lattice mismatch alignment similar to what was reported earlier corresponding to this (MoS_2-graphene) configuration. [13] The vdW c-space lattice constant obtained after geometry optimization yields a gap of ~ [3.36Å] interlayer spacing which is acceptable with in the vdW interaction range. From the preliminary observations of the TDOS of individual graphene, 1H-MoS_2 and the stack optimized with the DV 585 defect, it is clear that energy level renormalization or modification does take place with shifting of HOMO-LUMO energy bands closer to each other, which is rather different from the TDOS of either graphene with DV585 and 1H-MoS_2. The TDOS's have been adjusted with 0.6eV correction factor to match with the single layer band gap of 1H-MoS_2, which is 1.9 eV. Additionally we also explore the change in work function of the stack compared to 1H-MoS_2. Interestingly it is found that lowering of barrier potential or work function takes place in the stack (φ~5.07eV) with respect to 1H-MoS_2 (φ~5.44 eV). This also suggests that electronic band and its parameters does get modified due to stacking which could be useful for many optoelectronic applications.

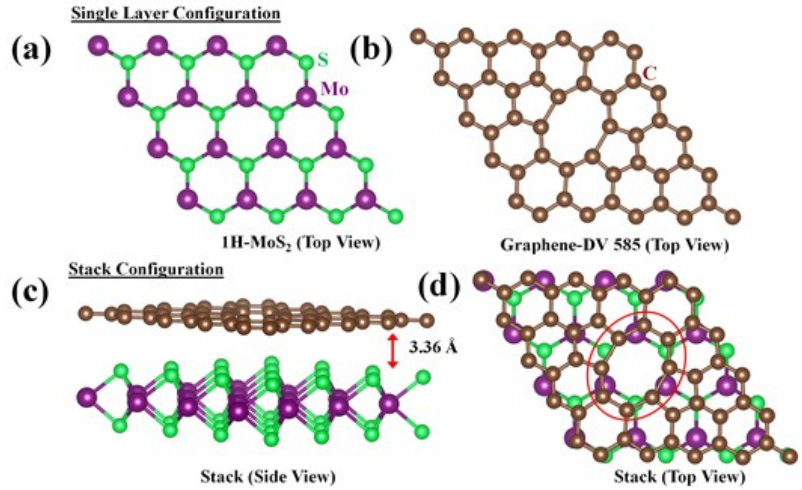

Figure S5: Optimized model of (a) infinitely large single layer graphene sheet with DV 585 defect (b) infinitely large single layer of MoS_2 sheet**.** Optimized structure of vdW heterostacked MoS_2-graphene sheet from (c) side and (d) top view

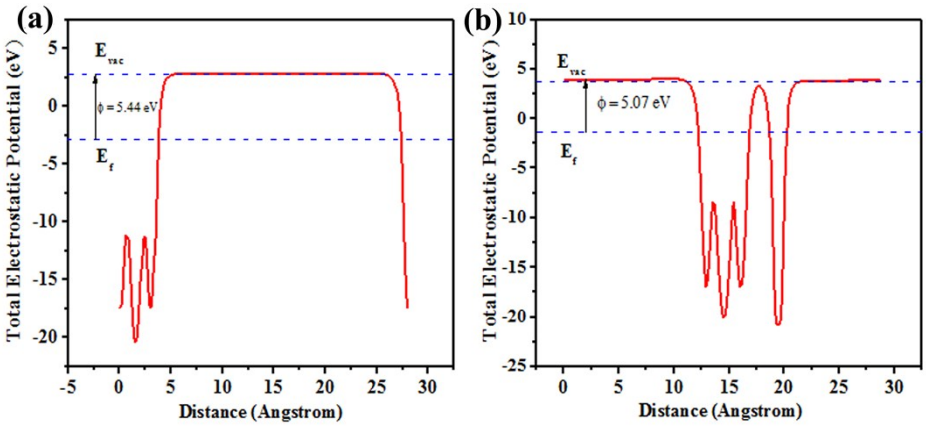

Figure S6: (a, b) Theoretical work function determined for single layer MoS_2 (5.44 eV) which reduced in the vdW heterostacked (graphene-MoS_2) configuration (5.07 eV)

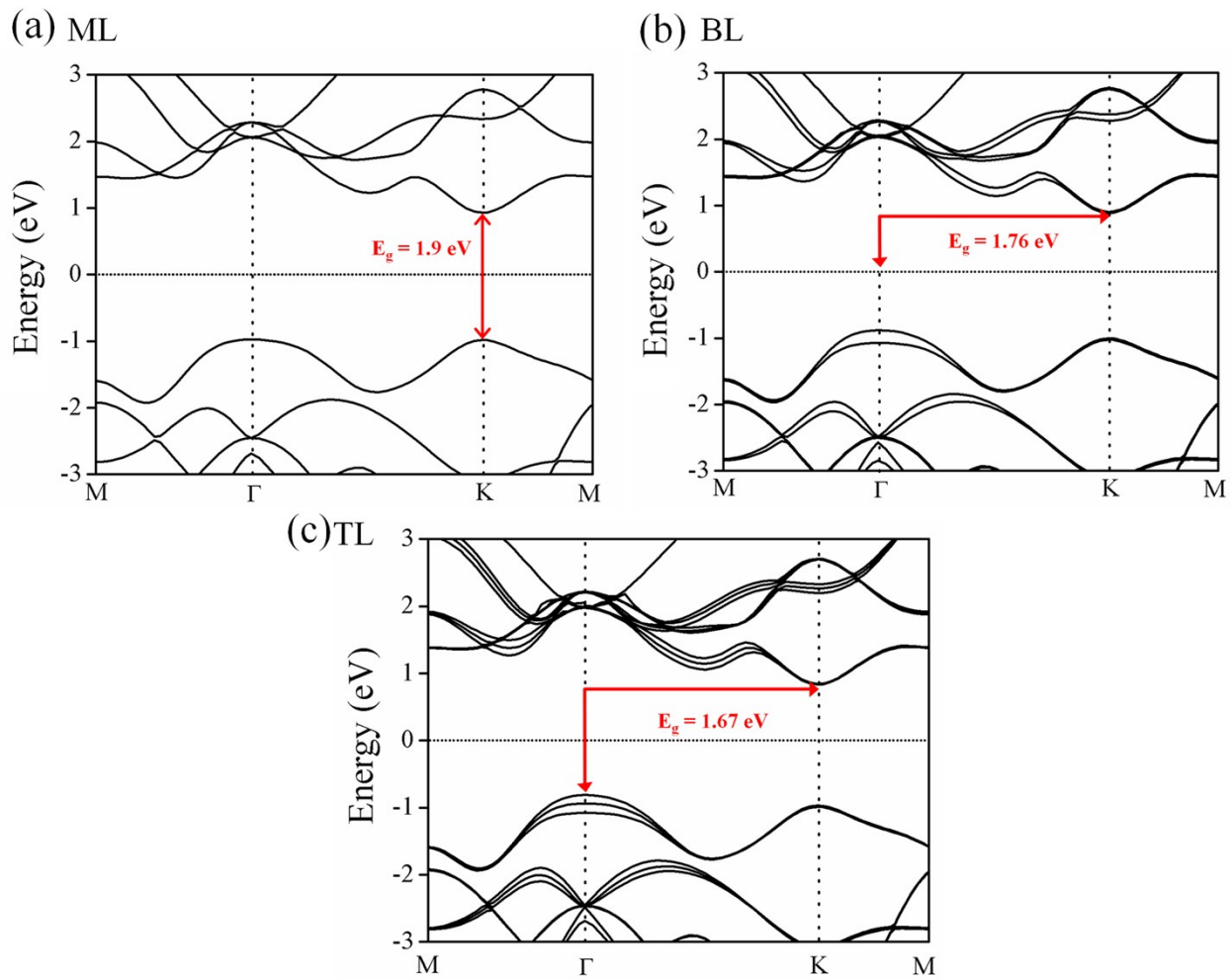

Figure S7: Depicting the *ab-initio* band structures of (a) monolayer (ML), (b) Bi-layer (BL) and (c) Tri-layer (TL) MoS_2 sheets and their evolution from direct to indirect band gap as layer no. increases

Direct band gap to indirect band gap nature is observed for monolayer to trilayer MoS_2 structure. The band gap value is varied from 1.90 eV to 1.67 eV for monolayer to tri layer MoS_2. Band of GQD consider in this work is 2.5 eV. Work function value is in decreasing order for monolayer to trilayer MoS_2 (5.44 eV, 5.42 eV, 5.38 eV for monolayer, double layer and triple layer). For the case of graphene quantum dot the work function is around 4.5 eV, as shown in figure S7 and figure S8. All calculations were conducted using PBE-PAW exchange correlation functional.

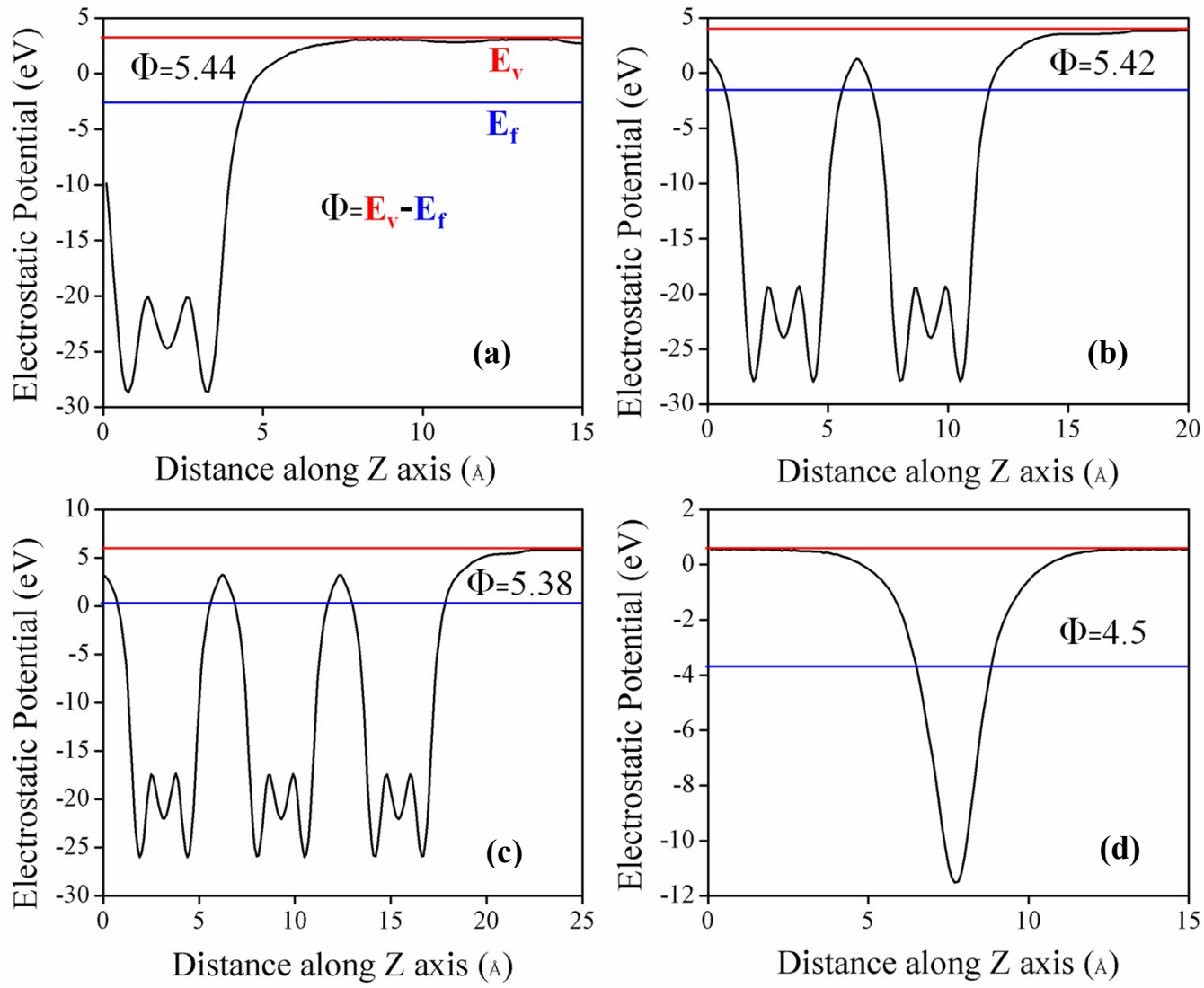

Figure S8: Depicting the *ab-initio* computed work function of (a) monolayer (ML), (b) Bi-layer (BL) and (c) Tri-layer (TL) MoS_2 sheets and (d) single GQD

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