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# Experimental and Theoretical Investigation of Synthesis and Properties of Dodecanethiol-functionalized $MoS_2$

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#### Abstract

Herein, we investigate the DDT (1-Dodecanethiol) functionalization of exfoliated  $MoS_2$  by using experimental and theoretical tools. For the functionalization of MoS<sub>2</sub>, DDT treatment was incorporated into the conventional NMP (N-methyl pyrrolidone) exfoliation procedure. Afterward, it has been demonstrated that the functionalization process is successful through optical, morphological and theoretical analysis. The D, G and 2LA peaks seen in the Raman spectrum of exfoliated NMP-MoS<sub>2</sub> particles, indicate the formation of graphitic species on  $MoS_2$  sheets. In addition, as the DDT ratio increases, the vacant sites on  $MoS_2$  sheets diminish. Moreover, at an optimized ratio of DDT-NMP, the maximum number of graphitic quantum dots (GQDs) is observed on MoS<sub>2</sub> nanosheets. Specifically, the STEM and AFM data confirm that GQDs reside on the  $MoS_2$ nano-sheets and also that the particle size of the  $DDT-MoS_2$  is mostly fixed, while the NMP-MoS<sub>2</sub> show many smaller and distributed sizes. The comparison of PL intensities of the NMP-MoS<sub>2</sub> and DDT-MoS<sub>2</sub> samples states a 10-fold increment is visible, and a 60-fold increment in NIR region photoluminescent properties. Moreover, our results lay out understanding and perceptions on the surface and edge chemistry of exfoliated  $MoS_2$ and open up more opportunities for MoS<sub>2</sub> and GQD particles with broader applications.

# 1 Introduction

Graphene, a two-dimensional (2D) and atom-thick carbon material has received great interest owing to its ultrahigh carrier mobility, thermal conductivity and mechanical strength.<sup>1,2</sup> As a member of 2D materials family, a group of layered materials such as transition metal dichalcogenides (TMD) has been studied widely due to their interesting thickness-dependent optical, electrical and mechanical characteristics.<sup>3</sup> In the past decade, TMDs such as molybdenum (IV) disulfide are used extensively in the form of nanostructures<sup>4</sup>, van der Waals heterostructures<sup>5</sup>, nanocomposites<sup>6</sup>, compositional heterojunctions<sup>7</sup>, 3D foams<sup>8</sup> and functionalized TMD nanosheets<sup>9</sup>.



Figure 1: A detailed synthesis route for the conventional liquid phase exfoliation and DDT-assisted exfoliation of MoS<sub>2</sub>.

In its base form, the bulk and non-luminescent  $MoS_2$ , gain access to its luminescent properties upon exfoliation.<sup>10,11</sup> The bulk crystal structure of  $MoS_2$  consists of weakly interacted 6.5 Å thick  $MoS_2$  layers with a van der Waals (vdW) gap, which allows multi-layered structures like  $MoS_2$  to be exfoliated. In general opinion, the  $MoS_2$  layers are accepted as chemically inert species, specifically, the basal sites of the vdW stacked layered composition of 2H- $MoS_2$ .<sup>12</sup> It seems logical that the broken bonds at the  $MoS_2$  layer edges would increase reactivity <sup>13</sup>, and it has been demonstrated that the edge sites of 2H- $MoS_2$  exhibit different electrical characteristics than those of the pristine basal plane.<sup>14</sup>

To further expand the utilization of  $MoS_2$  and to amplify the characteristics of interest towards desired applications, covalent and non-covalent basal and edge-plane functionalization have been utilized over the years. In doing so, a variety of functionalized- $MoS_2$  have been used throughout the last decade for the applications in solar cells, <sup>15</sup> catalysis, <sup>16</sup> sensors, <sup>17</sup> photodynamic/photothermal therapy, <sup>18,19</sup> biosensors, <sup>20</sup> tissue engineering, <sup>21</sup> and cell imaging. <sup>22</sup>

While functionalization provides a wide range of applications that are suit-

able for understanding the nature of absorption in different regions of the electromagnetic spectrum, it especially opens a door to many variations of diode and photoresponsive sensor device designs and structures.<sup>23</sup> In the field of advanced sensors, sensors with low detection limits are often nanoparticle-sensitized 2D materials and atomic-thick 2D materials have continued to attract great attention for specific parts of infrastructures of sensor devices. However, the enhancement of optical, electrical and thermal properties of MoS<sub>2</sub> continues at full speed today. The functionalization of  $MoS_2$  with organic molecules bearing thiol functional groups during exfoliation has been studied as a whole new area of thiol-conjugated transition-metal disulfides. However, in the case of 1-Dodecanethiol (DDT) functionalization, there is an insufficient number of studies that have been reported previously. For instance, Ahmad et al.<sup>24</sup> propose an optimized method that involves oleylamine (OLA) and DDT-assisted exfoliation procedures for the thinning of bulk  $MoS_2$ , which is utilized in a 2D/0Dhybrid of  $MoS_2/CuInS_2$  quantum dots. Park et al.<sup>25</sup> report a facile method for enhancement of chemically exfoliated 1T-MoS<sub>2</sub>, by annealing and simultaneously treating with DDT molecules in the presence of, therefore exchanging Mo-O with Mo-S bonds. In both of these works, a formation of heterostructure with a treatment of DDT have proved a 5-fold increase in photoluminescence in visible region. In the aforementioned previous studies examining the functionality of  $MoS_2$  with DDT, the unintentionally generated quantum dots of the sonication-assisting solvent were not mentioned. In this study, both the interaction of quantum dots with  $MoS_2$  and the role of self-assembly monolayer formed of DDTs were investigated.

In this study, motivated by the recent cost-effective synthesis of low-dimensional TMDs, we propose a mechanism of functionalization of  $MoS_2$  via the DDT molecule. DLS size analysis showed that there is a formation of heterostructure in the system when DDT is involved. AFM and STEM analysis gave insight into the orientation of the heterostructure formed, which is residual GQDs on  $MoS_2$  particles. A thorough analysis based on DFT simulations, for bare and functionalized heterostructures of  $MoS_2$ , is in agreement with the proposed infrastructure of the heterostructure.

# 2 Material and methods

#### 2.1 Experimental procedure

Synthesis of NMP-MoS<sub>2</sub> Exfoliated Suspension: Suspensions with a concentration of 10 mg/mL were prepared by mixing 100 mg of MoS<sub>2</sub> bulk powder (Sigma-Aldrich, 98%) with 10 mL of N-methyl-2-pyrrolidone (Sigma-Aldrich) and the mixture is sonicated with the probe-tip sonication method. The sonication procedure consists of a 20-minute sonication of the sample with a pulse of 7 s on and 5 s off and a power of 130 W. The dispersion acquired from sonications was centrifuged (Nuve, NF1215) at 5000 rpm for 2 hours to discard the bulk MoS<sub>2</sub> from separated MoS<sub>2</sub> layers.



Figure 2: (a) Raman spectrum of dry NMP-MoS<sub>2</sub> on Si/SiO<sub>2</sub> substrate, excited with the laser of 785 nm. (b) Binding energies of NMP, in different molecule pairs and Molecular Dynamics (MD) simulation snapshot at 5000 K of liquid NMP solvent on Vienna ab-initio Simulation Package (VASP) software. (c) UV-Vis absorption spectrum of the as-exfoliated liquid NMP-MoS<sub>2</sub> sample. (d) Photoluminescence spectrum of the liquid NMP-MoS<sub>2</sub> sample, excited with 535, 540, 545 and 550 nm excitation wavelengths. (e) AFM image and and cross section height profile and (f) AFM particle size distribution of NMP-MoS<sub>2</sub> on Si/SiO<sub>2</sub> substrates. (g) Bright-field STEM images of exfoliated NMP-MoS<sub>2</sub> samples. (h) DLS size distributions of NMP-MoS<sub>2</sub> and sonicated bare NMP samples.

Synthesis of DDT-MoS<sub>2</sub> Bulk Suspension: Suspensions with a concentration of 100 mg/mL were prepared by mixing 100 mg of MoS<sub>2</sub> bulk powder (Sigma-Aldrich, 98%) with 1 mL of 1-Dodecanethiol (Sigma-Aldrich, 98%) and stirring the suspension for 3 hours at 70 degrees Celsius, then keeping the flask stirred for 20 hours at room temperature afterward, at ambient.

Synthesis of DDT-MoS<sub>2</sub> Exfoliated Suspension: After the preparation of the DDT-MoS<sub>2</sub> precursor, the suspension is put in a beaker and mixed with 9 ml of NMP. This DDT-NMP-MoS<sub>2</sub> mixture is sonicated with the probe-tip sonication method. The sonication procedure consists of a 20-minute sonication of the sample with a pulse of 7 s on and 5 s off and a power of 130 W. During the sonication, to avoid overheating of both the dispersion and tip-probe sonicator and stabilize the sample at the desired temperatures, an ice-bath is employed for every 10 minutes of sonication. (Nanolinker, NL650) The dispersion acquired from sonications was centrifuged (Nuve, NF1215) at 5000 rpm for 2 hours to discard the bulk MoS<sub>2</sub> from separated MoS<sub>2</sub> layers. Afterward, the suspension is purified by adding excess acetone and discarding the organic phase. The summary and schematic of the procedure are given in Fig. 1.

Cleaning of  $SiO_2/Si$ : Commercial SiO<sub>2</sub>(300 nm)/Si substrates were first cleaned via Piranha solution and rested in DI water. Then, bath-sonication was employed onto SiO<sub>2</sub>/Si substrates for 10 minutes in acetone, ethanol (EtOH), and isopropanol (IPA) for the removal of the solvent residues, respectively, and the substrates were dried via N<sub>2</sub> purging. Thereafter, the exfoliated DDT-MoS<sub>2</sub>, NMP-MoS<sub>2</sub> and sNMP suspensions were drop-cast onto the sterilized SiO<sub>2</sub>/Si substrates and put in a vacuum oven to remove solvent residues.

Characterization: Absorbance and photoluminescence (PL) spectra were acquired using the HORIBA Duetta with a Xenon light source with a power of 75 W. Before the measurements, MoS<sub>2</sub> dispersions in IPA and NMP were held in a quartz cell during optical analysis, and the background correction was performed by placing a quartz cell filled with NMP. Raman Spectroscopy analyses were conducted with a Raman Microscope (HORIBA, XploRA PLUS) under ambient conditions, with an operating wavelength of 785 nm and a spectral resolution of 1 cm<sup>-1</sup>. The calibration was performed with the Si peak at 520 cm<sup>-1</sup>. Bright field Scanning Transmission Electron Microscope (STEM) images were taken on Si/SiO<sub>2</sub> substrates. STEM images were taken by implementing a transmission detector in FEI, QUANTA 250 FEG with an accelerating voltage of 15 kV. Atomic Force Microscopy (AFM) images were taken on Si/SiO<sub>2</sub> substrates (Bruker-MMSPM Nanoscope 8). Dynamic Light Scattering measurements are done in NMP solvent (Malvern Panalytical, ZetaSizer).

#### 2.2 Theory and calculation

First-principle density functional theory (DFT) calculations were performed with Vienna ab-initio Simulation Package using projector augmented wave (PAW) potentials.<sup>26–28</sup> The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-correlation functional.<sup>29</sup> The van der Waals interactions were included by utilizing the DFT-D2 method of Grimme.<sup>30</sup> The geometric relaxation of atoms set to come to a halt when pressures in all directions were less than 1 kB. Brillouin zone sampling was performed with automatic k-point meshes. For the hexagonal unit cell, a grid of  $3 \times 3 \times 1$  was used, and the k-point grid scales with the supercell dimensions. To avoid interaction between vicinal monolayers, a vacuum spacing of at least 10 Å was taken. For achieving geometric relaxation, the convergence criterion was established as a total energy difference of  $10^{-5}$  eV between consecutive computational steps involving electronic and structural adjustments. For the density of states (DOS) calculations, a Gaussian smearing width of 0.05 eV was used.

# 3 Results and discussion

#### **3.1** Exfoliation of MoS<sub>2</sub> in NMP

While there are rapid developments in the synthesis of nanoscale materials, a reliable characterization of the obtained products is also of importance. Considering this need, vibrational spectroscopy stands out as a simple and effective method. Therefore, we first investigate the Raman characteristics of the exfoliated  $MoS_2$  samples.

The Raman spectrum shown in Fig. 2(a) can be divided into two main regions: (i) MoS<sub>2</sub> regions extend between 370 and 460 cm<sup>-1</sup> and (ii) the byproduct region between 1250 and 1650 cm<sup>-1</sup>. In the MoS<sub>2</sub> region, there are three prominent Raman active phonon branches. While the  $E^{1}_{2g}$  peak at 378 cm<sup>-1</sup> originates from the in-plane out-of-phase vibration of Mo and S atoms,  $A_{1g}$  at 403 cm<sup>-1</sup> is due to the out-of-plane vibration of S atoms. In addition, 2LA peak located around 450 cm<sup>-1</sup> emerges as a result of the second-order Raman process involving the longitudinal acoustic phonon at the M point of the Brillouin Zone.<sup>31</sup> The Raman spectrum reveals that, differing from the  $E^{1}_{2g}$  and the  $A_{1g}$  peaks, the 2LA branch has an anti-symmetric shape nature due to its multi-phononic nature.

Moreover, the high-frequency phonons appearing in the Raman spectrum of  $MoS_2$  crystals obtained by chemical exfoliation are also noteworthy. It is known that during the probe sonication process, the probe tip heats its surroundings to extreme temperatures by generating alternating series of low and high-pressure waves in the solvent.<sup>32</sup> Therefore, one can expect NMP solvent to undergo dramatic structural modifications such as polymerization and isomerization during the solvothermal synthesis processes.<sup>33</sup> Our calculations reveal that, as shown in Fig. 2(b), NMP molecules in a vacuum interact with one another via hydrogen-type bonds with a binding energy of 70 meV. In addition, the hydration of NMP significantly enhances intermolecular interactions to the order of 600 meV. Moreover, the binding energy of each NMP on the  $MoS_2$  surface is calculated to be 770 meV without any charge transfer. Despite the fact that the formation of strong covalent bonds between NMP molecules or the host  $MoS_2$  lattice is not expected, clusterization of NMPs on the basal plane of  $MoS_2$  is likely to happen. In addition, MD calculations (performed for



Figure 3: (a) Computed theoretical binding energy values of the interactions of pristine  $MoS_2$ -DDT, sulfur-vacant (SV)  $MoS_2$ -DDT, zigzag (ZZ) and armchair (AC) edge sites of  $MoS_2$  with the both ends of the DDT molecule. (b) AFM image and and cross section height profile and (c) AFM particle size distribution of DDT-MoS<sub>2</sub> bundles (red) and particles (blue) on Si/SiO<sub>2</sub> substrates. Measured bundles in AFM size distribution are marked with black dashed lines in the AFM image. (g) Bright-field STEM images of exfoliated DDT-MoS<sub>2</sub> samples. (e) DLS size distribution of DDT-MoS<sub>2</sub> samples.

temperatures from 0 to 5000 K in 5 ps) show that bond dissociation in NMP molecules and the formation of various carbon-based clusters take place starting from 4250 K. Therefore, it can be deduced that the carbon-based particles formed by carbonization of NMP molecules are GQDs and the peaks located at the vicinity of 1350 cm<sup>-1</sup>, 1600 cm<sup>-1</sup> and 2635 cm<sup>-1</sup> are attributed to D, G and 2D peaks, respectively, of graphitic materials.

For further characterization of the obtained composite material, absorption and photoluminescence measurements are also performed. Fig. 2(c) shows that the absorption peak<sup>34</sup> of MoS<sub>2</sub> exfoliated in NMP solvent is at 2.45 eV. While the absorption edge correlates with the peaks between 550 and 700 nm in the visible region in the photoluminescence spectrum (Fig. 2(d)), the shifting behavior of peaks according to the energy of the excitation laser confirms that the photoluminescent particles are in the form of quantum dots. However, it is clear that the source of the PL peaks around 1000 nm is the GQDs, rather than MoS<sub>2</sub> crystals, that emerge during sonication. Moreover, recently, both the theoretical investigation on the size and shape-dependent luminescent properties, and synthesis-application of NIR-luminescent GQDs are studied and discussed in detail in previous studies.<sup>35</sup>

The 2D AFM topographical image shown in Fig. 2(e) reveals that the sonication of MoS<sub>2</sub> yields agglomerated islands of particles. The height profiles of

	1	
$\mathbf{E}_b(\mathbf{eV})$	$\mu(\mu_B)$	$ ho(\mathbf{e})$
0.77	0.0	0.01
0.07	0.0	0.00
0.40	0.0	0.03
0.60	0.0	0.02
0.70	0.0	0.04
0.68	0.0	0.00
0.95	0.0	0.02
0.69	0.0	0.00
2.67	4.0	0.20
0.91	0.0	0.00
2.31	0.0	0.10
0.82	0.0	0.00
1.28	0.0	0.00
1.32	0.0	0.01
1.25	0.0	0.01
1.23	0.0	0.00
0.18	0.0	0.00
0.39	0.0	0.01
0.23	0.0	0.04
0.07	0.0	0.00
0.04	0.0	0.00
	$E_b(eV)$ 0.77 0.07 0.40 0.60 0.70 0.68 0.95 0.69 2.67 0.91 2.31 0.82 1.28 1.32 1.25 1.23 0.18 0.39 0.23 0.07 0.04	$\mathbf{E}_b(\mathbf{eV})$ $\mu(\mu_B)$ $0.77$ $0.0$ $0.07$ $0.0$ $0.07$ $0.0$ $0.40$ $0.0$ $0.60$ $0.0$ $0.60$ $0.0$ $0.68$ $0.0$ $0.95$ $0.0$ $0.69$ $0.0$ $2.67$ $4.0$ $0.91$ $0.0$ $2.31$ $0.0$ $1.28$ $0.0$ $1.23$ $0.0$ $1.23$ $0.0$ $0.18$ $0.0$ $0.39$ $0.0$ $0.23$ $0.0$ $0.04$ $0.0$

Table 1: A data sheet to identify the fashion of complex formation (the binding energies of DDT to GQDs and H<sub>2</sub>O by the thiol and methyl terminal sites of the molecule.) and the binding of the DDT on different sites of MoS<sub>2</sub> layers. Possible net magnetic moments  $\mu_{net}$  are given in Bohr magneton. Charge transfer  $\rho$  is the amount of electron transfer between the components of the related system.

the particles along the marked sections demonstrate a height of 10-40 nm. The AFM size distribution data in Fig. 2(f) shows that the exfoliated NMP-MoS<sub>2</sub> particles vary in the range of 50-150 nm as well. When the AFM image is examined closely, it is seen that the individual particles have grain boundaries, and this implies the particles' formation happens through agglomeration of smaller particles. In the STEM image shown in Fig. 2(g), the smaller GQD particles appear to be scattered around MoS<sub>2</sub> nanoflakes. According to the DLS analysis in Fig. 2(h), the 1-2 nm particles correlated in the STEM image are the result of bare NMP sonication, which is related to the GQD formation. Moreover, in the aqueous phase, NMP-MoS<sub>2</sub> is dispersed rather than agglomerated. Therefore, the sizes of NMP-MoS<sub>2</sub> seem to be much lower (around 10 nm) than in the AFM results.

#### **3.2** Functionalization by Dodecanethiol

Understanding how 2D crystalline materials can be functionalized and what properties they can acquire when they are functionalized is important in terms of finding more uses in technological applications. In this context, functionalization of  $MoS_2$  crystals by means of thiol-based organic molecules such as DDT stands out as a cheap and effective method due to its sulfurous structure.<sup>36,37</sup>

A reliable prediction of how  $MoS_2$  crystals interact with DDT molecules during the experimental functionalization process can be achieved with DFTbased calculations. As shown in Fig. 3(a), the binding energy of DDT on defectfree  $MoS_2$  surface is 0.70 eV from the sulfur side and 0.68 eV from methyl side of the molecule. Bader analysis shows that DDT molecules tend to form strong bonds without charge transfer, regardless of which ends they approach the  $MoS_2$ crystal. In addition, the occurrence of structural defects in the experimental synthesis and transfer process is inevitable, and the most prominent among these are sulfur vacancies.<sup>38</sup> For the S-vacant state, the binding energy of the DDT molecules from the methyl end increases slightly to 0.69 eV. However, the interaction energies of the sulfuric ends of DDT molecules on S-vacant regions of  $MoS_2$  increase dramatically up to 0.95 eV. It seems that even if there are structural defects that occur in the  $MoS_2$  crystal during the sonication with NMP, the defect-induced electronic and optical instability can be eliminated by the non-covalent DDT-functionalization.

AFM and DLS analyses demonstrate that  $MoS_2$  crystals synthesized by exfoliation method mostly consist of flakes ranging in size 50-100 nm and also reveal that in addition to basal plane, interaction of DDT molecules with edges must also be taken into account. As shown in Fig. 3(a), the interactions of DDT molecules with the zigzag and armchair edges of  $MoS_2$  were investigated. It is seen that each DDT interacts with the zigzag edge with a binding energy of 0.91 eV (2.67 eV) from its methyl (sulfur) side. Similarly, for armchair edges of  $MoS_2$  flakes binding energy per DDT molecule is calculated to be 0.82 eV (2.31 eV) from its methyl (sulfur) side. Apparently, it is reasonable to assume that while the basal plane of  $MoS_2$  is functionalized through strong S-S interactions, the edges are theoretically expected to be terminated via partly covalent-ionic binding between the Mo atom of the edge and the S atom of the DDT.

The AFM analysis of DDT-functionalized  $MoS_2$  is shown in Fig. 3(b-c). What appears at first glance in the AFM image is the relatively large yellow spots appearing on large fragments. Particle size analysis clearly reveals that both GQDs and  $MoS_2$  flake sizes increase in the presence of DDT. In addition, STEM analysis presented in Fig. 3(c-d) also shows that the synthesized DDT- $MoS_2$  bundles appear as large flakes. Based on the DLS data in Fig. 3(e), quantum dots of 50-100 nm are adsorbed on  $MoS_2$  flakes with an average length of 275 nm (Fig. 2(h) and Fig. 3(e)). Here it is seen that the presence of DDTs provides a strong interaction of both ends of the DDT molecules and the  $MoS_2$  edges results in larger  $MoS_2$  fragments. This strong interaction can be further hinted by changed zeta potential values of systems. While NMP- $MoS_2$  has a zeta potential of 4 mV, DDT-functionalized  $MoS_2$  has a zeta potential of -7 mV. Therefore, our experimental results show that the surface charge of different samples are changed negligibly.

Additionally, since the emergence of GQDs in the sonication-based exfoliation process is inevitable, it is of importance to understand how they interact with DDT molecules. For simulation, the GQDs are modeled as a 10 Å long and 4 Å wide sp<sup>2</sup> hybridized 2D carbon planes. As shown in Fig. 4, the binding energy of DDT with the basal plane of GQD is 1.28 eV from its sulfur side and 1.32 eV from methyl side. It is also seen that DDT molecules strongly interact with the edges of GQDs with a binding energy of 1.23 (1.25) eV from their methyl (sulfur) side. Therefore, although the DDT-GQD interactions are energetically favorable, there is no absolute distinction between the different sites of adsorption of DDT onto the GQDs. Moreover, to examine the formation of micelle-like structures and the effect of moisture DDT-DDT and DDT-H<sub>2</sub>O interactions are also investigated theoretically. DDT-DDT interaction is calculated to be 0.18 eV (0.39 eV) for parallel (anti-parallel) orientation of DDT molecules. Furthermore, while H<sub>2</sub>O molecules weakly bind to the hydrogenated sites of the DDT molecule bonding is quite large (0.23 eV) at the sulfur side of the DDT molecule. It is clear that the surfaces of GQDs are tightly surrounded by DDTs during the functionalization process. It can be inferred that the GQD-DDT clusters are able to form micelle-like structures by strongly interacting with water molecules from their sulfide ends.

The Raman measurement showing the vibrational spectra of DDT-functionalized  $MoS_{2}s$  is presented in the Fig. 5. First of all, for 532 nm laser excited Raman measurements (Fig. 5(a)), it is seen that the  $(E^{1}_{2g} \text{ and } A_{1g})$  peaks of  $MoS_{2}$  appear at 383 and 409 cm<sup>-1</sup>, respectively. Moreover, prominent peaks of  $MoS_{2}$  dispersed in DDT-NMP 1:9 (DDT-NMP 5:5) emerge at 380 (383) and 406 (409) cm<sup>-1</sup>. For 785 nm laser excited Raman measurements (Fig. 5(b)), it is seen that the increase in the number of DDT molecules leads to hardening in the prominent phonon modes of  $MoS_{2}$ . While dispersed  $MoS_{2}$  via NMP exhibit Raman lines at 378 and 403 cm<sup>-1</sup>, respectively, the peaks of  $MoS_{2}$  dispersed in DDT-NMP 1:9 (DDT-NMP 5:5) emerge at 380 (380) and 405 (406) cm<sup>-1</sup>.

Such phonon hardening, which occurs as a result of strong interaction of DDT molecules with the  $MoS_2$  surfaces, is clearly associated with the reduction



Figure 4: Calculated binding energy values of the interactions of GQD-DDT(SH), GQD-DDT(CH<sub>3</sub>), DDT parallel and anti-parallel, GQD(edge)-DDT(CH<sub>3</sub>), GQD(edge)-DDT(SH), DDT(CH<sub>3</sub>)-H<sub>2</sub>O, DDT(SH)-H<sub>2</sub>O and DDT(side)-H<sub>2</sub>O coordinations of active molecules in experimental media. Values of interaction energies are calculated in the order of GGA.



Figure 5: The Raman spectra of NMP-MoS<sub>2</sub> and different ratios of DDT-NMP of DDT-MoS<sub>2</sub> functionalized samples on Si/SiO<sub>2</sub> substrates.



Figure 6: (a) Photoluminescence (PL) spectra of the liquid NMP-MoS<sub>2</sub>, functionalized DDT-MoS<sub>2</sub> and GQDs samples, excited with 535, 540, 545 and 550 nm wavelengths. (b) Schematic representations of NMP-MoS<sub>2</sub> and DDT-MoS<sub>2</sub> systems. (c) Energy level alignment diagrams for the interface between MoS<sub>2</sub>, GQD and DDT in a heterojunction.

in the crystal lattice.<sup>39</sup> Another finding in the Raman spectrum of DDT-MoS<sub>2</sub> (Fig. 5(b)) is that the intensity of the edge and defect-induced 2LA phonon mode decreased gradually with the increasing amount of DDT in the media. Apparently, defect healing and edge termination of  $DDT-MoS_2$  particles can be monitored via 2LA phonon branch. In addition, vibrational characteristics of GQDs show that while DDT functionalization leads to a remarkable increase in phonon intensities, negligible shift in their phonon frequencies is observed. The intensity ratio of D/G hints to the character of a defective graphitic material. The high frequency Raman lines exhibit approximate ratios of 0.76 to 0.93 for the 532 nm laser, and 0.92 to 1.48 for the 785 nm laser which is evident in previous studies that these D/G ratios correspond to a range of GQD structures including various variations of graphene oxide<sup>40</sup>. Apparently, the vibrational characteristics of both  $MoS_2$  particles and GQDs change with functionalization. It is seen that higher amounts of DDT in the sample cause decent increases in the D/G ratio measured with both lasers, therefore hinting at a distortion in graphitic species' crystallinity or less likely, saturation of sp<sup>2</sup>-hybridized carbons upon additional DDT treatment. Therefore, while this trend implies lower crystallinity in graphitic region upon DDT treatment, it also confirms the tight interaction of GQDs and DDT molecules.

For optical characterization of the functionalized crystal structures, the photoluminescence spectra of NMP-MoS<sub>2</sub>, DDT-MoS<sub>2</sub> and GQDs are also given in Fig. 6(a). It is seen that the intensity of  $MoS_2$  originated PL peaks is significantly enhanced due to the DDT functionalization. Similarly, the PL intensities of GQDs stimulated in the high wavelength region are increased by up to 60-fold with the effect of DDT functionalization. Here, the peak positions displaying dependence on the excitation wavelength indicate that the DDT-covered luminescent particles are still in the form of quantum dots. Here, the DDT-induced increase in the optical visibility of functionalized products requires explanation. As schematized in the Fig. 6(b), the surfaces of  $MoS_2$  and GQD are coated with DDT, resulting in spatial separation between these two material groups. Therefore a reasonable theoretical explanation of enhanced PL intensity can be obtained by employing Anderson's rule used for the construction of energy band diagrams of the heterojunctions. For confirmation of Anderson's rule hypothesis, the bandgaps of are calculated for each party as they are modeled in the paper previously (MoS<sub>2</sub> as in Fig. 3, GQDs as in Fig. 4). As the calculated bandgaps are shown in the Fig. 6(c), absence of DDTs, the interface obtained by the combination of GQDs and  $MoS_2$  materials forms a type-II heterojunction. Upon excitation, the lowest possible energy state (LUMO) for electrons in this heterostructure originates from  $MoS_2$ , while the highest energy level (HOMO) where holes can be found originates from GQDs. Therefore, the PL intensity obtained from excitations in a such heterojunction is low. However, it is seen that the HOMO states of DDT molecules have lower energy than the HOMO (VBM) states of GQDs (MoS<sub>2</sub>) and its LUMO state lies at a higher energy level than the band edge of GQDs and  $MoS_2$ . Therefore, it can be concluded that the binary structures of GQDs, MoS<sub>2</sub> dots and DDT are type-I heterostructures and the PL intensity is enhanced in these structures where excitation and recombination processes occur on the same type of material.

# 4 Conclusion

In this work, one-pot synthesis of dodecanethiol (DDT) functionalized  $MoS_2$  was performed, and obtained heterostructures were further investigated in terms of their morphological, optical and vibrational properties by both experimental and theoretical tools. For the purpose of performed functionalization, DDT treatment was incorporated into the traditional NMP-exfoliation process. It was shown that the process yields strong binding of DDT to the basal plane and edges of  $MoS_2$ , as corroborated by the theoretical binding-energy calculations. The functionalized nanostructures of DDT-MoS<sub>2</sub> yielded 60- and 10-fold photoluminescence for NIR and Visible regions, respectively. While the damped 2LA phonon modes were attributed to the DDT-functionalization, we found that the photoluminescence enhancement is caused by the formation of type-I heterostructure with the DDT encapsulation.

Our study focuses on whether  $MoS_2$ , a well-known two-dimensional crystal, can acquire new functions by interacting with simple organic molecules. The

experimental data obtained not only showed that the DDT molecule effectively functions the  $MoS_2$  crystal, but also revealed that carbon-based solvents such as NMP used during the sonication processes also lead to the formation of nanomaterials that can play a functional role. The resulting  $MoS_2$  crystals were found to exhibit enhanced optoelectronic properties.

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