Dual Functionalization of Liquid-Exfoliated Semiconducting 2H-MoS₂ with Lanthanide Complexes Bearing Magnetic and Luminescence Properties

Simon G. McAdams, Edward A. Lewis, Jack R. Brent, Sarah J. Haigh, Andrew G. Thomas, Paul O’Brien,* Floriana Tuna,* and David J. Lewis*

Liquid exfoliated, atomically thin semiconducting transition metal dichalcogenides (TMDs), as inorganic equivalents of graphene, have attracted great interest due to their distinctive physical, optoelectronic, and chemical properties. Functionalization of 2D TMDs brings new prospects for applications in optoelectronics, quantum technologies, catalysis, and medicine. In this report, dual functionalization of 2D semiconducting 2H-MoS₂ nanosheets through simultaneous incorporation of magnetic and luminescent properties is demonstrated. A facile method is proposed for tuning the properties of the TDM semiconductors and accessing multimodal platforms, consisting in covalent grafting of lanthanide complexes onto the surface of 2D TMDs. Dual functionalization of liquid-exfoliated MoS₂ nanosheets is demonstrated simultaneously with both europium (III) and gadolinium (III) complexes to form a coloidally stable luminescent (with millisecond lifetimes) and paramagnetic MoS₂-based nanohybrid material. This work is the first example of transition metal dichalcogenide nanosheets functionalized with preformed lanthanide complexes. These findings open new prospects for covalent functionalization of TMDs with molecular species bearing specific functionalities as a means to tune the optoelectronic properties of the semiconductors, in order to create advanced materials and devices with a wide range of functionalities.

1. Introduction

2D materials are at the center of intense research for a range of next-generation devices in, for example, energy storage, electronics, and sensing applications, due to their tunable physical, optoelectronic, and chemical properties.[1] These features arise from the anisotropic effects of the materials when thinned toward monolayers.[2] Of particular interest is the use of 2D materials as multimodal platforms for biomedical applications.[3] Most notably, transition metal dichalcogenides (TMDs) are a versatile alternative to the archetypal 2D nanomaterial graphene, with MoS₂, for example, displaying a higher near-infrared absorption compared with graphene oxide, which is attractive for photothermal therapy.[4] Various TMDs and oxides have been employed in multimodal biomedical applications such as MnO₂,[5] TiS₂,[6] and WS₂.[7] However, the majority of TMD multimodal platforms utilize MoS₂ to combine photothermal therapy with drug delivery[8] or use MoS₂/Bi₂Se₃ as a dual diagnostic/therapeutic agent.[9]

Direct functionalization of MoS₂ nanosheets is a potentially convenient and controlled route to multimodality. Thiol-containing molecules are typical ligands used to functionalize MoS₂ nanosheets via binding to sulfur vacancies in the host lattice.[10] Previous work has functionalized MoS₂ with dimer-captosuccinic-acid-coated Fe₃O₄ nanoparticles for magnetically targeted phototherapy and magnetic resonance imaging (MRI),[11] and disulfide-containing polyethylene glycol to create stable MoS₂ aqueous dispersions for photothermal therapy with drug delivery.[12] In these studies, MoS₂ nanosheets were chemically exfoliated by lithiation to produce the metallic 1T-MoS₂ polymorph, which shows little photoluminescence.[13] In contrast, the bulk 2H-MoS₂ polymorph is a semiconductor with an indirect band gap of 1.2 eV, while the monolayer form has a direct band gap of ≈1.8 eV.[14] Such a tunable band gap has attracted significant research in view of optoelectronic applications compared to graphene, which has no band gap in its native form.[15] Grafting molecules to the surface of such 2H-MoS₂ monolayers are of interest as it allows to modulate the
optical and electronic properties of the semiconductors, due to changes in the electronic structure of MoS2, and to introduce new functionalities. Moreover, binding of mercapto acids to defect sites of 2H-MoS2 was found to improve dispersion of the monolayers in water.[16] Similarly, reaction of liquid-exfoliated 2D MoS2 with M(OAc)2 salts (M = Ni, Cu, Zn; OAc = acetate) allowed for its dispersion/processing in more conventional laboratory solvents, while furnishing the 2H-polytype of MoS2, which is a semiconductor.[17] Attempts to covalently functionalize 2H-MoS2 with organic molecules featuring thiol groups have given contradictory results. Some studies claim that the thiols bind covalently to the molybdenum ions of 2H-MoS2 at S-atom vacancies, but the Mo–S interaction was not fully investigated.[16] In other studies, X-ray photoelectron spectroscopy (XPS) provided evidence for the oxidation of organic thiols to disulfides and thus their potential physiadsorption to 2H-MoS2 instead of coordinative linkage.[18] However, binding of dibenzo- thiophene to S-atom vacancies on small MoS2 clusters was unarguably confirmed by high-resolution scanning tunneling microscopy.[19] In addition, edge sites of 2H-MoS2 nanosheets were recently covalently functionalized with 1,2-dithiolanes.[20]

Functionalization of 2H-MoS2 nanosheets with lanthanide complexes is attractive due to the varied luminescent and paramagnetic elements the rare earths possess. For example, Gd3+ with seven unpaired electrons and a slow magnetic relaxation is typical of a MRI contrast agent, while Eu3+ and Tb3+ have narrow emission bands for optical imaging and long photoluminescence lifetimes (in the millisecond timescale).[21] The latter is useful for biological imaging as signals can be gated to avoid organic fluorescence from proteins and DNA, which occur on the nanosecond timescale. Nanoparticles have been used as platforms for binding lanthanides,[22] with one example anchoring both Eu and Gd simultaneously onto a silica nanoparticle surface,[23] building on previous work by Lewis et al. who used gold nanoparticles as a scaffold for the assembly of lanthanide(III) complexes.[24] In comparison, there are few examples that exist of nanosheets as platforms for lanthanide complexes. Graphene has been functionalized with either Gd(III) or Tb(III) complexes,[25] and with Eu(III) nanoparticles.[26] Recently, MoS2 was exfoliated using cysteamine, and reacted with DTPA- dihydrate (DTPA = diethylenetriaminepentaacetic acid) to form a Gd(III) chelate.[27] Additionally, the MoS2 nanosheets agglomerated during exfoliation with cysteamine to form large spheres, eventually forming a core–shell-like structure when reacted with Gd3+. Additionally, the functionalization of MoS2 with cysteamine caused a phase transition from the 2H-MoS2 to the 1T-MoS2 phase.

In this paper, we demonstrate that it is possible to covalently functionalize atomically thin 2H-MoS2 nanosheets simultaneously with Eu(III) and Gd(III) complexes to form a novel 2D luminescent and paramagnetic multimodal material (Scheme 1). The 2D structure of the MoS2 nanosheets was maintained post-functionalization, and we demonstrate that they exhibit sensitized luminescence from Eu3+ as well as the paramagnetism of Gd3+.

2. Results and Discussion

MoS2 nanosheets were prepared from bulk MoS2 powder exfoliated in 2-propanol as previously described by Backes et al.[28] The dispersions were analyzed using atomic force microscopy (AFM) (Figure 1). Low-resolution AFM scans revealed a limited number of larger sheets (N = 21) with a mean 30 nm height and 182 nm diameter (Figure 1a) and a unimodal distribution. High-resolution scans (Figure 1b,c) revealed the majority of sheet heights as 1.45 ± 0.43 nm (N = 1715) (Figure 1d), indicative of a bilayer structure (one sheet is ≤0.7 nm).[29]

The ligand N,N′-bis(µ-thiophenylamido) diethylenetriamine-N,N′,N′-triacetic (H3L) was prepared as previously described by Lewis et al.[24b] (through a condensation reaction between 4-aminothiophenol and DTPA- bis(anhydride), and was reacted with GdCl3·xH2O or EuCl3·xH2O to afford GdL and EuL, respectively. For functionalization of nanosheets, a 5 mL MoS2 dispersion (2-propyl alcohol, 0.25 mg mL−1) was mixed with 5 mL of a methanolic solution of EuL (20 µmol) or 5 mL EuL/GdL solution (in methanol, 10 µmol of each complex) and sonicated for 3 h. The hybrid material was isolated and washed with methanol through three rounds of centrifugation. The final pellet was resuspended in methanol to form a stable colloid for further characterization.

The optical properties of MoS2@LnL were investigated in detail. UV–vis absorption spectra of MoS2@LnL show a peak at 269 nm, which is not present in the as-synthesized MoS2 nanosheets, and is assigned to the π→π* transitions of the thiophenylamide groups of the grafted EuL and GdL (Figure 2a).[28a] The shift of the 266 nm peak for EuL to 269 nm for the functionalized MoS2@LnL material could potentially reflect the different chemical environment of the thiophenylamide group once grafted to the MoS2 surface. Importantly, the well-defined absorption peaks of MoS2 at 618 and 677 nm, ascribed to the A1→E transitions of the thio- phenylamide groups of the grafted EuL and GdL (Figure 2a). The shift of the 266 nm peak for EuL to 269 nm for the functionalized MoS2@LnL material could potentially reflect the different chemical environment of the thiophenylamide group once grafted to the MoS2 surface. Importantly, the well-defined absorption peaks of MoS2 at 618 and 677 nm, ascribed to the A and B direct exciton transitions,[29] are only present in the 2H-MoS2 phase, and are indeed absent in the 1T-MoS2 phase.[13,18a] MoS2@EuL and MoS2@EuL/GdL show similar absorbance maxima at 615 and 676 nm. Hence, we conclude that the 2H-MoS2 does not undergo a phase change during functionalization as others have reported.[18a,27]

Steady-state emission spectra and luminescence lifetimes were recorded for both MoS2@EuL and MoS2@EuL/GdL (Figure 2b). The luminescence lifetimes of the 3D0 → 7F2 transition at ~613 nm of Eu3+ were similar for both MoS2@LnL adducts and comparable to the value of 0.8 ms reported for
This indicates that no quenching pathways are introduced by attaching the Eu(III) complex to the surface of the MoS2 nanosheets and that the lanthanide ion most likely preserves its coordination environment. Steady-state emission spectra ($\lambda_{\text{exc}} = 270$ nm) showed the $5D_0 \rightarrow 7F_J$ ($J = 0, 1, 2, 3, 4$) emission lines of Eu$^{3+}$ to be present in both MoS$_2$@EuL and MoS$_2$@EuL/GdL samples, indicating that the presence of Gd$^{3+}$ does not alter Eu$^{3+}$ emission (Figure 2c). These results are significant as they demonstrate that the desired luminescence characteristics of the Eu$^{3+}$ ions (i.e., sharp line-like emission with long lifetimes, compared with organic luminophores) are retained after binding. As the excitation wavelength (266 nm) is commensurate with the $\pi-\pi^*$ transition of the ligand, this is further evidence that the structural integrity of the complex is not compromised upon binding to MoS$_2$, and indeed the population of the lanthanide excited state proceeds through the triplet state of the ligand, as observed previously by Lewis et al.[24a]

MoS$_2$@EuL and MoS$_2$@EuL/GdL were imaged using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) with energy dispersive X-ray (EDX) spectrum mapping. Figure 3 shows that the Mo, Eu, and Gd signals are spatially colocalized, confirming that EuL and GdL are associated with the MoS$_2$ nanosheet surface (see Figure S2 in the Supporting Information for a line-scan profile). We note an increase in Eu and Gd signal intensity at the edge of the MoS$_2$ (Figure S2, Supporting Information), possibly due to preferential binding of thiolated ligands to MoS$_2$ edge sites, as described by others.[10,31] In HAADF-STEM images of MoS$_2$@EuL, Mo and Eu signals also colocalize (Figure S3, Supporting Information). EDX sum spectra from imaging demonstrated the expected ratio of Mo:S (1:2), with Eu and Gd at a level of $0.5 \pm 0.2$ at% and $0.5 \pm 0.2$ at% (i.e., $\approx 1:1$), respectively, in MoS$_2$@EuL/GdL; and Eu at $0.5 \pm 0.1$ at% in MoS$_2$@EuL (see Table S1 for tabulated results, including inductively coupled plasma mass spectrometry (ICP-MS), and Figure S4 in the Supporting Information for 1D-EDX spectrum).

To investigate the nature of the thiol–MoS$_2$ interaction, XPS was performed. Recently McDonald and co-workers investigated this interaction on MoS$_2$ nanosheets functionalized with cysteine, and while the free thiol (S-H) peak was absent in the Fourier transform-infrared red spectrum, XPS showed clear evidence that a disulfide cystine formed during the functionalization process.[18a] Figure 4 shows the XPS spectra of Mo 3d, Eu 3d, and S 2p core levels. The binding energy of Mo and S in MoS$_2$@EuL is consistent with crystalline 2H-MoS$_2$, with Mo$^{4+}$ 3d$_{5/2}$ and Mo$^{3+}$ 3d$_{3/2}$ doublets observed at 229.2 and 232.4 eV, respectively. S 2s appears at 226.4 eV,[12a] The S 2s peak of EuL is at a higher binding energy of 227.7 eV, indicative of the
different chemical environment compared to the bound thiol (S-Mo). A limited Mo$^{6+}$ (MoO$_3$) component was also observed at 235.64 and 232.55 eV in MoS$_2$@EuL, possibly due to a small amount of surface oxidation or dangling edge sites. Eu$^{3+}$ 3d$_{5/2}$ peaks appeared in both MoS$_2$@EuL and EuL at 1135 eV, with both samples showing characteristic multiplet split Eu$^{3+}$ 3d$_{5/2}$ peaks at 1143 and 1125 eV. Importantly, the S2p doublet peaks shifted from 164.7 and 163.5 eV for EuL, which has unbound SH groups, to 163.4 and 162.1 eV in MoS$_2$@EuL, in agreement with existence of thiolate–Mo bonds. A similar trend was reported by Tagmatarchis and co-workers for surface functionalization of exfoliated 2H-MoS$_2$ with 1,2-dithiolane bearing an ethylene glycol alkyl chain with a pyrene moiety, concluding that the 2S$_{p}$ XPS peaks of functionalized MoS$_2$ and bulk MoS$_2$ were comparable. There was no indication of a free thiol component or a disulfide component in the XPS spectrum of MoS$_2$@EuL. Fourier-transform infrared (FT-IR) spectroscopy of MoS$_2$@LnL showed no S–H stretch, which further confirms the absence of a thiol component (Figure S5, Supporting Information).

We note that the distance between the two pendant sulfur groups of LnL is 0.6–0.7 nm, which is ≈2a of the MoS$_2$ crystal (≈0.6 nm) and is commensurate with binding. The inductively coupled plasma optical emission spectrometry (ICP-OES) results presented in the Supporting Information suggest that the actual stoichiometric formula of the material produced is MoS$_{1.73}$ Ln$_{0.02}$. Further evidence of 2H-MoS$_2$ thiolation comes from Raman spectroscopy; the E$_{2g}$ and A$_{1g}$ modes of MoS$_2$@LnL were shifted by 3 cm$^{-1}$ to higher wavenumbers, compared to the as-synthesized MoS$_2$ nanosheets (Figure S6, Supporting Information). A similar shift in MoS$_2$ Raman modes was reported by Cho et al. after passivating mechanically exfoliated MoS$_2$ with alkanethiols.

The paramagnetism of solid state MoS$_2$@EuL/GdL and GdL was confirmed using Q-band electron paramagnetic resonance (EPR) spectroscopy at 298 K (Figure 5). The EPR spectrum...

Figure 2. Optical characterization of MoS$_2$, EuL, MoS$_2$@EuL, and MoS$_2$@EuL/GdL in methanol. a) Ultraviolet visible absorption spectrum. b) Fluorescence lifetime spectrum. c) Steady-state emission spectrum ($\lambda_{\text{exc}} = 270$ nm). Spectra were normalized according to the area under the $^5$D$_0 \rightarrow ^7$F$_2$ emission. All spectra were corrected for instrument response.

Figure 3. HAADF-STEM with EDX spectroscopy of MoS$_2$@EuL/GdL. a) HAADF-STEM image with corresponding EDX maps of b) Mo, c) Eu, and d) Gd.
of the GdL complex showed a single resonance peak due to Gd$^{3+}$ with $S = 7/2$, $g = 1.99$, and a negligible zero-field splitting (zfs) term. MoS$_2$@EuL/GdL showed a similar resonance peak, thus confirming the paramagnetism of the hybrid material. The broader EPR signal may result from small distortions in the coordination geometry of the Gd$^{3+}$ ion upon grafting to MoS$_2$. Indeed, the EPR spectrum of MoS$_2$@EuL/GdL requires zfs terms of 1575 and 100 MHz (Figure S7, Supporting Information). Unfunctionalized MoS$_2$ does not show a broad signal but only a weak sharp resonance at $g = 2.00$. A similar resonance peak was observed by others in 2H-MoS$_2$ nanosheets, and was attributed to sulfur vacancies.$^{[37]}$ Additional resonance peaks, such as those found in 1T-MoS$_2$ ($g = 1.93$),$^{[37]}$ are absent, which further confirms the purity of the 2H-MoS$_2$ phase. Furthermore, MoS$_2$@EuL/GdL showed a relatively strong paramagnetic response in comparison to unfunctionalized 2H-MoS$_2$ (Figure S8, Supporting Information), consistent with the presence of paramagnetic Gd$^{3+}$.

3. Conclusions

In conclusion, liquid exfoliated 2H-MoS$_2$ nanosheets were covalently functionalized simultaneously with Eu$^{III}$ and Gd$^{III}$ complexes, with the luminescent and paramagnetic properties of the respective lanthanides being maintained post functionalization, in addition to the semiconductor 2H-MoS$_2$ nanosheet phase. These results represent the first example of preformed lanthanide complexes being covalently linked to 2H-MoS$_2$ nanosheet surfaces, and offer a broad approach to synthesizing transition metal chalcogenide nanosheets with molecular functionality that draw from the varied luminescent and paramagnetic properties the rare earths possess. Furthermore, this approach can be applied to bind lanthanide single-molecule magnets,$^{[38,39]}$ and even molecular spin qubits$^{[40]}$ to the surface of semiconducting 2D TMDs, allowing fabrication of devices that will exploit their peculiar magnetic bistability and/or quantum properties.$^{[41]}$

4. Experimental Section

**General:** All materials and chemicals were purchased from Sigma-Aldrich, and used as received.

**Preparation of H$_2$L and LnL (Ln = Gd or Eu):** N,N’-Bis[1-thiophenyl(aminocarbonyl)]diethylene-triamine-N,N’,N’-triacetic acid (H$_2$L) was synthesized through a previously reported procedure.$^{[26]}$ H
NMIR (400 MHz, MeOH-d₄), δ ppm: 7.24 (4H, d, J = 8.75 Hz); 6.985 (4H, d, J = 8.75 Hz, H₂); 4.23 (2H, s); 3.52 (4H, s, H₂); 3.49 (4H, s, H₂); 3.41 (4H, t, J = 5.43 Hz); 3.22 (4H, t, J = 5.34 Hz) (Figure S1, Supporting Information). Anal. Calcld. for C₉₂H₁₃₂N₂O₆S₂(N₁₂H₁₂)(ClO₄)₂: C 44.2, H 5.8, N 12.3. Found: C 44.1, H 5.6, N 12.9. GdL and EuL were synthesized as previously described.[24b] H₃L (0.25 g, 0.40 mmol) and LnCl₃·6H₂O (0.40 mmol) were dissolved in degassed methanol (3 mL) with mild sonication. LnL precipitated as a white powder with the addition of acetonitrile (30 mL), and was collected via suction filtration under N₂. The complex was washed with acetonitrile (30 mL) and diethyl ether (30 mL), dried under vacuum, and finally stored under nitrogen at −18 °C. GdL: MS (ES-TOF) m/z: 763 [M+H]+. EuL: MS (ES-TOF) m/z: 758 [M+H]+.

Preparation of MoS₂@LnL (Ln = Gd or Eu): MoS₂ nanosheets were prepared from bulk MoS₂ powder exfoliated in 2-propanol alcohol as previously reported by Backes et al.[13] 100 mL of 2H-MoS₂ powder in isopropl alcohol (20 mg mL⁻¹) was aliquoted into 10 mL glass vials, which were then placed in a sonicator bath (37 kHz, 30% power) for 24 h (Scheme S1, Supporting Information). The solution was centrifuged at 1500 rpm for 45 min in 2 x 50 mL falcon tubes. The top 35 mL of each tube was carefully aliquoted and stored for further characterization. The final concentration of the MoS₂ suspension was 0.25 mg mL⁻¹. 5 mL MoS₂ suspension in isopropl alcohol (0.25 mg mL⁻¹) was mixed with EuL (5 mL methanol, 20 µmol) or EuL/GdL (5 mL methanol, 10 µmol) of each and sonicated (37 kHz, 30% power, room temperature (RT)) for 3 h. The hybrid material was isolated and washed with methanol through three rounds of centrifugation (10 000 rpm). Then, the final pellet was responded in methanol (3 mL).

Characterization Techniques: High resolution TEM imaging, HAADF-STEM imaging, and EDX imaging were performed using a probe side aberration corrected FEI Titan G2 80-200 S/TEM “ChemiSTEM” instrument operating at 200 kV. EDX spectra and spectrum images were analyzed using Bruker Esprit software. STEM images were analyzed using Catan Digital Micrograph software. Samples were prepared by dropping dilute nanoparticle solution onto a carbon-coated copper grid. EDX quantification was performed with the Bruker Esprit software using the Cliff-Lorimer approach and with no absorption correction. ICP-MS measurements were performed at the University of Manchester School of Earth, Atmospheric and Environmental Sciences. Raman spectroscopy was performed using a Renishaw RM system 1000 Raman spectrometer with a 514 nm laser. AFM measurements were performed using a Bruker Multimode 8 instrument with a silicon-nitride tip. EPR spectra were recorded in continuous-wave mode with a Bruker EMX 300 EPR spectrometer operating at a microwave frequency of 34 GHz (Q-band) at 298 K. Simulations were performed using EasySpin software with MATLAB.[42] Magnetic studies were performed using a Quantum Design PPMS-XL SQUID magnetometer equipped with a 7-tesla magnet. Hysteresis curves were recorded at 2 K by cycling the magnetic field between (7 T) and (−7 T) fields (sequence used: (0) → (7 T) → (−7 T) → (7 T)). UV-vis absorption spectra were collected using a double beam UV-1800 Shimadzu UV–vis spectrophotometer between 200 and 900 nm. Samples were measured in quartz cuvettes with a path length of 1 cm, and pure solvent was used as a blank. Photoluminescence (PL) emission spectra were collected using a GILDEN Photonics fluoroSENS spectrofluorometer at a 270 nm excitation wavelength, with a 1 nm resolution. Quantum yields were measured using an integration sphere (Edinburgh Instruments).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was supported by the EPSRC UK North-West Nanoscience Doctoral Training Centre (NoWNano DTC), EPSRC grant EP/G03737X/; the EPSRC UK National EPR Research Facility and Service at the University of Manchester; and the EPSRC UK grants EP/M022498/1, EP/ K016946/1, and DTRA (HDTRA1-12-1-0013).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
2D materials, lanthanide complexes, magnetic properties, metal dichalcogenides, multifunctionality

Received: July 3, 2017
Revised: July 31, 2017
Published online:


