

Comparison of MoS₂, WS₂ and Graphene Oxide for DNA Adsorption and Sensing

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Abstract

Interfacing DNA with two-dimensional (2D) materials has been intensely researched for various analytical and biomedical applications. Most of such studies were performed on graphene oxide (GO), and two metal dichalcogenides, MoS₂ and WS₂; all of them can all adsorb single-stranded DNA. However, they like use different surface forces for adsorption based on their chemical structures. In this work, fluorescently labeled DNA oligonucleotides were used and their adsorption capacity and kinetics were studied as a function of ionic strength, DNA length and sequence. Desorption of DNA from these surfaces were also measured. DNA is more easily desorbed from GO by various denaturing agents, while surfactants yield more desorption from MoS₂ and WS₂. Our results are consistent with that DNA can be adsorbed by GO via π - π stacking and hydrogen bonding, MoS₂ and WS₂ mainly use van der Waals force for adsorption. Finally, fluorescent DNA probes were adsorbed by these 2D materials for detecting the complementary DNA. For this assay, GO gave the highest sensitivity, while they all showed a similar detection limit. This study has enhanced our fundamental understanding of DNA adsorption by two important types of 2D materials and is useful for further rational optimization of their analytical and biomedical applications.

Introduction

Nanomaterials for DNA adsorption are useful for delivering therapeutic nucleic acids,¹ designing smart stimuli-responsive materials,^{2,3} and developing biosensors.⁴⁻⁶ In particular, two-dimensional (2D) materials have recently emerged as a unique platform for interfacing with DNA. Compared to traditional nanoparticles, 2D materials often have a larger specific surface area. Developments in this field was stimulated by the discovery of graphene.⁷ To disperse in water and interface with biopolymers, graphene oxide (GO) is often used.⁸⁻¹⁰ The interaction between GO and DNA has been extensively studied,¹¹⁻¹⁵ which has inspired the exploration of various other 2D materials. Among them, MoS₂ and WS₂ are two representative examples.¹⁶⁻¹⁹ Using these two materials for DNA-based sensing was reported with simple DNA oligonucleotides,²⁰⁻²⁷ as well as aptamers,^{28, 29} and DNAzymes.³⁰ Thiolated DNA was also attached to AuNPs to improve sensing based the intrinsic photoluminescence property of MoS₂.³¹ Adsorption of DNA improves the colloidal stability of MoS₂ nanosheets,³² and DNA can even exfoliate WS₂,³³ suggesting a strong interaction.

Aside from these applied research, only a few fundamental studies were reported. Theoretical work pointed out that van der Waals (vdW) force is mainly responsible for DNA base adsorption by MoS₂ and WS₂.^{34,35} A comparison was made for DNA adsorption on these materials using fluorescently labeled magnetic nanoparticle probes.³⁶ MoS₂, WS₂ and GO can all adsorb single-stranded (ss) DNA while repel double-stranded (ds) DNA.³⁷ By examining their chemical structures, one can readily see that MoS₂ and WS₂ are quite different from GO. For example, GO can adsorb DNA via pi-pi stacking with DNA bases, while MoS₂ and WS₂ are non-aromatic.

Given the increasing importance of these 2D dichalcogenide materials for DNA functionalization, a systematic surface science study and in particular a side-by-side comparison with GO is critical, which is the main goal of this study.

Materials and Methods

Chemicals. All the DNA samples were purchased from Integrated DNA Technologies (Coralville, IA). The DNA sequences are as follows. T₁₅ refers to TTTTTTTTTTTTTTTT; FAM-T₁₅ refers to labeling a carboxyfluorescein on the 5'-end of T₁₅; FAM-24mer: FAM-ACGCATCTGTGAAGAGAACCTGGG; and c-24mer: CCCAGGTTCTCTTCACAGATGCGT. All the sequences are listed from the 5' to 3'. Carboxyl GO, monolayer molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂) were from ACS Material (Medford, MA). Sodium chloride, sodium hydroxide, sodium carbonate, sodium bicarbonate, magnesium chloride, adenosine, 4-morpholineethanesulfonate (MES), tris(hydroxymethyl)aminomethane (Tris), and 4-(2-hydroxyethyl) piperazine-1-ethanesulfonate (HEPES) were from Mandel Scientific (Guelph, Ontario, Canada). Dimethyl sulfoxide (DMSO), sodium dodecyl sulfate (SDS), cetyl trimethylammonium bromide (CTAB), Tween 80, and Triton X-100 were from Sigma-Aldrich. Milli-Q water was used for all the experiments.

TEM, UV-vis, and ζ -potential measurement. The MoS₂, WS₂ or GO nanosheets were directly dispersed in Milli-Q water. TEM was performed on a Philips CM10 transmission electron microscope. The sample was prepared by pipetting a drop of the aqueous dispersion (200 $\mu\text{g/mL}$ for MoS₂ and WS₂, 100 $\mu\text{g/mL}$ for GO) onto a 230 mesh copper holey carbon grid and then dried in air. The electronic absorption of MoS₂ and WS₂ (100 $\mu\text{g/mL}$) and GO (25 $\mu\text{g/mL}$) was obtained by a UV-vis spectrometer (Agilent 8453A). The ζ -potential (50 $\mu\text{g/mL}$ materials in 10 mM acetate, phosphate or carbonate buffer to cover the full pH range) was measured by dynamic light scattering

on a Malvern Zetasizer Nano ZS90 with a He-Ne laser (633 nm) at 90 degree collecting optics at 25 °C.

DNA adsorption. The kinetics of DNA adsorption was studied by adding different concentrations of MoS₂, WS₂ or GO to 50 µL solution containing 50 nM FAM-labeled DNA in buffer A (20 mM Tris, pH 7.0, 100 mM NaCl, 2 mM MgCl₂) at 25 °C. Several different salt concentrations were also tested. The fluorescence was measured on a microplate reader (Infinite F200 Pro, Tecan) with 490 nm excitation and 520 nm emission.

Sensor preparation. A solution of 500 µL containing MoS₂ (2 mg/mL), WS₂ (5 mg/mL) or GO (0.1 mg/mL) was respectively incubated with 500 nM FAM-A₁₅ in buffer A in dark at room temperature for 1 h. Then these solutions were washed with buffer A by centrifugation at 15,000 rpm for 10 min. The sensors were finally dispersed in 500 µL buffer A and stored at 4 °C (named solution I, II and III respectively).

DNA desorption. To study DNA desorption induced by chemicals, 5 µL solution I, II or III was respectively centrifuged. After removing the supernatant, the pellets were respectively dispersed in 50 µL of 5 M urea, 10 mM NaOH, 10 mM phosphate, 1 mM adenosine solution, 3 M NaCl, or 50% DMSO. The fluorescence intensity was measured immediately. The background fluorescence was measured by dispersing the same samples in 50 µL buffer A. For surfactant-induced DNA desorption, each well contained 45 µL buffer A and 5 µL solution I, II and III. Then different concentrations of SDS, Tween 80, Triton X-100, or CTAB were added to induce desorption.

DNA sensing. For DNA sensing with MoS₂, WS₂ or GO, each well contained 45 µL buffer A and 5 µL solution I, II or III. Then different concentrations of the cDNA were added to initiate the reaction. Displacement of adsorbed DNA probes was studied using a similar method and a final

of 1 μM of A₁₅ or T₁₅ DNA without a fluorophore label was added. The FAM-24mer DNA was tested following the same protocol.

Results and Discussion

Materials characterization. Single-layered MoS₂ and WS₂ have a similar structure with the transition metal atoms covered on both sides by sulfur (Figure 1A). Therefore, the chance of DNA interacting directly with the metal centers is quite low except for the edges. While the sulfur atoms are fully exposed, they are not known to interact strongly with DNA. For comparison, GO has a diverse range of oxygen-containing moieties such as hydroxyl, epoxy and carboxyl groups (Figure 1B), allowing hydrogen bonding in addition to pi-pi stacking with DNA.

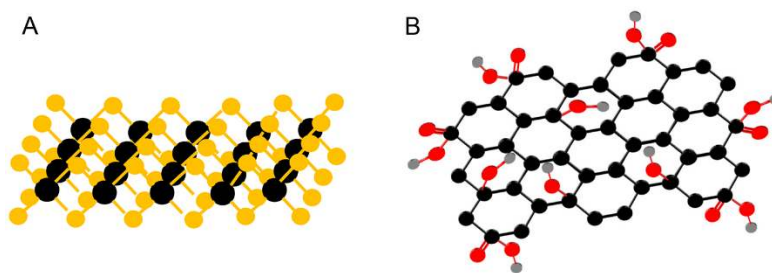


Figure 1. (A) The structure of a single-layered MoS₂ or WS₂. The Mo or W atoms are in black and the sulfur atoms are in yellow. (B) The structure of GO showing rich oxygenated groups: the carbon atoms in black, oxygen in red, and hydrogen in grey.

When dispersed in water at 0.5 mg/mL, MoS₂ is dark green, WS₂ is brown, while GO appears black (inset of Figure 2A). The UV-vis spectra of these samples are shown in Figure 2A. MoS₂ has a peak at ~ 420 nm and another one at >600 nm, explaining the green color. The absorption features of the other two are less obvious. To characterize their morphology, we performed TEM (Figure 2C-E). Each material appears as large micrometer sized sheets, consistent

with their 2D structure. Their similar 2D feature makes it ideal for a side-by-side comparison of their DNA adsorption property.

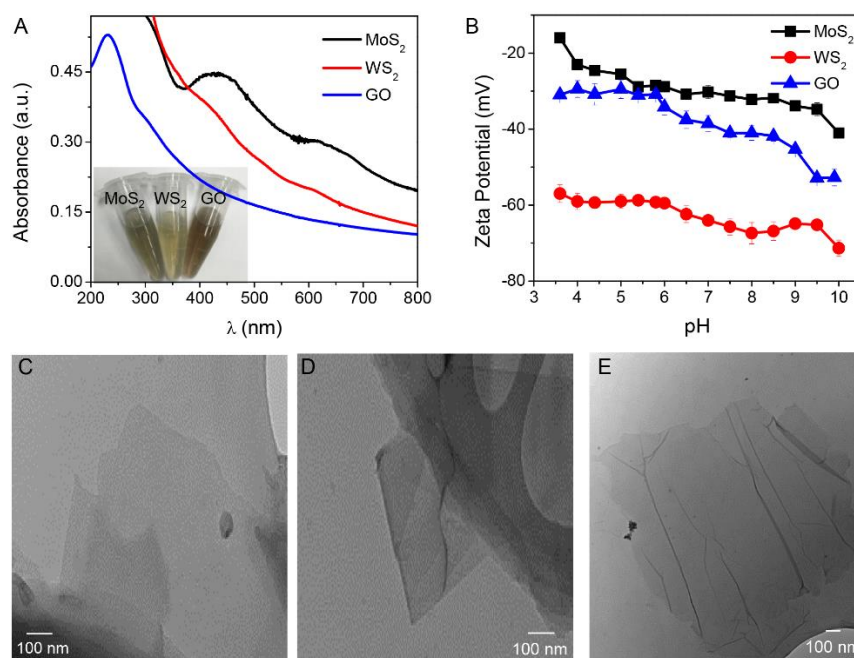


Figure 2. Characterization of these three 2D materials. (A) UV-vis spectra of MoS₂ and WS₂ (100 $\mu\text{g/mL}$) and GO (25 $\mu\text{g/mL}$) dispersed in water. Inset: a photograph of these materials (0.5 mg/mL each). (B) Zeta-potential of each material (0.05 mg/mL) as a function of pH in 10 mM buffer (acetate from pH 3.6 to 6; phosphate from pH 6 to 8.5; and carbonate from pH 9 to 10). TEM micrographs of (C) MoS₂, (D) WS₂ and (E) GO.

Since DNA is a highly negatively charged polymer, electrostatic interaction is likely to be important for its adsorption. As such, we measured the zeta-potential of each material as a function of pH (Figure 2B). From pH 3.5 to 10, all these materials are negatively charged. GO has surface carboxyl groups responsible for the negative charges.^{14,38} The negative charges on MoS₂ and WS₂ are attributable to the surface sulfur atoms.³⁹ Such negative zeta-potentials afford a reasonable

colloidal stability in aqueous dispersion. The zeta-potential of WS₂ is much more negative than the other two, and we indeed noticed a better colloidal stability of WS₂ than that of MoS₂.

DNA adsorption. Since DNA adsorption is the first step of interaction, we studied it first. As both DNA and these 2D materials are negatively charged, salt concentration might strongly affect adsorption. Using the FAM-A₁₅ DNA, we monitored its background fluorescence for 15 min and then respectively added each material (Figure 3A-C). In the absence of salt, no fluorescence quenching was observed, suggesting the lack of adsorption. With 100 mM NaCl, quenching occurred in all the samples. Further adding 2 mM Mg²⁺ resulted in even faster and stronger quenching in each case. Our results are consistent with that salt is required to overcome electrostatic repulsion for DNA adsorption. In addition, all these materials can quench fluorescence, which is useful for analytical applications.^{20, 21, 40}

We also noticed that at the same materials and salt concentration, GO induced the highest amount of quenching. To quantitatively understand this, we fixed the DNA and salt concentration, and monitored fluorescence quenching as a function of materials concentration (Figure 3D-F). In each case, a higher concentration induced more significant fluorescence quenching. With 20 μg/mL of GO, full adsorption was achieved, while it takes much more of MoS₂ and WS₂. We plotted the relative fluorescence quenching as a function of materials concentration (Figure 3G). At low concentration, a linear fluorescence quenching was observed. We attribute this mainly to adsorption, and the amount of fluorescence drop due to light scattering/absorption by these materials was neglected. The slopes of these curves represent the adsorption capacity at the experimental condition. We calculated that the capacity of GO is 36.6 times higher than that of MoS₂, and 33.0 times higher of WS₂.

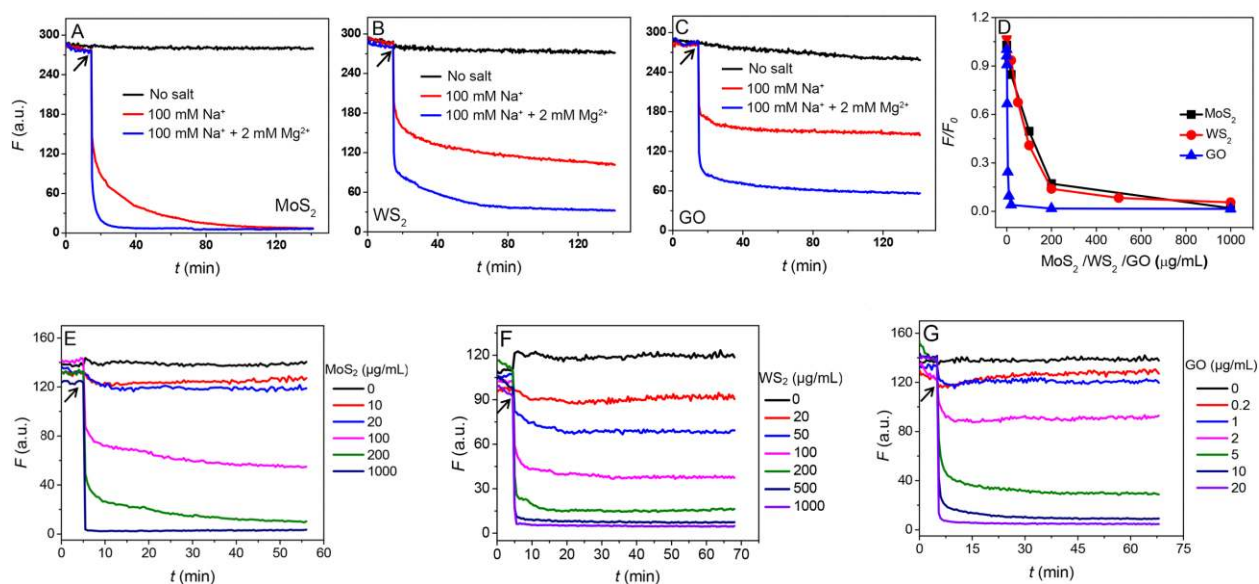


Figure 3. Kinetics of FAM-labeled A₁₅ (50 nM) adsorption by (A) MoS₂ (200 µg/mL), (B) WS₂ (500 µg/mL) and (C) GO (10 µg/mL) at three different salt concentrations. The materials were added at 15 min indicated by the arrowhead. (D) Relative fluorescence quenching as a function of materials concentration. The initial slope indicates the relative adsorption capacity. Kinetics of the DNA (50 nM) adsorption by various concentrations of (E) MoS₂, (F) WS₂ and (G) GO in buffer (100 mM NaCl, 2 mM Mg²⁺, 20 mM Tris, pH 7.0).

GO has a much lower molecular weight (made mainly of carbon and oxygen). With the same mass concentration, GO has a larger geometric surface area. The theoretical surface area is 2630 m²/g for a single graphene sheet. With oxygenated groups present, the surface area of GO is smaller than the theoretical graphene value. The oxygen content of our GO is about 40%,¹⁴ leading to a theoretical specific surface area of ~1575 m²/g. The surface area of the dichalcogenides are smaller since they contain heavier atoms. MoS₂ can reach 210 m²/g,⁴¹ and WS₂ is around 100 m²/g.⁴² This difference in specific surface area can account for a large fraction of the difference in DNA adsorption capacity. In addition, GO might have a higher adsorption affinity, allowing more

DNA to be adsorbed. For example, only GO can form pi-pi stacking and strong hydrogen bonding, while the other two materials cannot. The adsorption affinity might account for the rest of difference in adsorption capacity, and this is the topic of the subsequent section.

DNA desorption. To compare adsorption affinity and to understand the mechanism of DNA adsorption, we next studied DNA desorption. For this purpose, a FAM-labeled DNA was pre-adsorbed to prepare an adsorption complex with a low fluorescence. We monitored its background for a few minutes to ensure stable adsorption. Then a DNA denaturing agent was added to induce DNA desorption and the kinetics of fluorescence enhancement was followed. For each sample, we compared the fluorescence intensity with the free DNA in the buffer but without adding nanomaterials to calculate the desorption percentage. Each denaturing agent was used to probe a type of intermolecular force.

It is known that hydrogen bonding plays an important role in DNA adsorption by GO, which was supported by urea washing.⁴³ Following this, we exposed these three adsorption complexes to 5 M urea (Figure 4A). We observed a significant release of DNA from GO (>50%) but much less from the other two materials. This suggests that DNA adsorption by MoS₂ and WS₂ is independent of hydrogen bonding. This is reasonable since no hydrogen bond donors are on these materials and the ability of sulfur to be a hydrogen bond acceptor is much weaker than oxygen due to the low electronegativity of sulfur.

Next, the effect of pH was studied (Figure 4B). In this case, a final of 10 mM NaOH was added to each sample to raise the pH. Fluorescence enhancement was observed in all the samples, and GO had the highest fluorescence increase and thus the most DNA desorption. In general, at higher pH, the surface of these materials becomes more negative (Figure 2B). This would increase the electrostatic repulsion with DNA and weakening adsorption. Hydrogen bonding can also be

disrupted at high pH due to deprotonation of hydrogen bond donors, which may explain the more desorption from GO. We did not try acidic pH since low pH would increase the adsorption affinity,⁴⁴ and thus no desorption is expected.

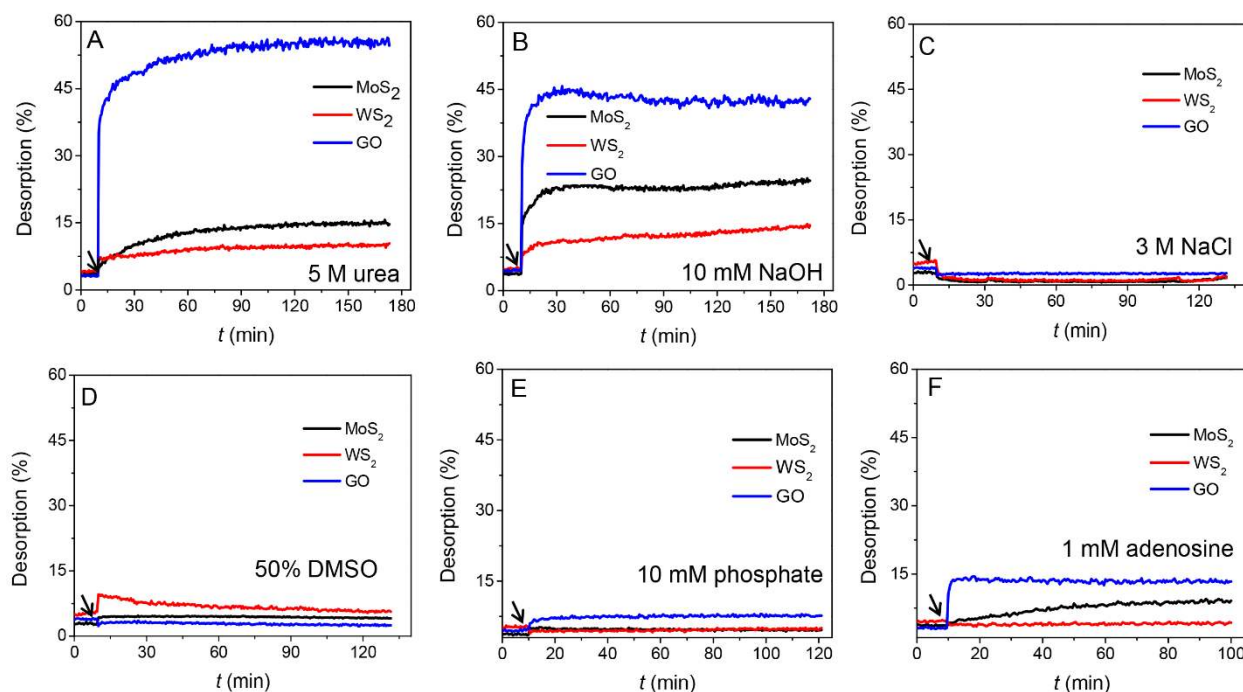


Figure 4. Comparison of DNA desorption from MoS₂, WS₂ and GO under various denaturing conditions. Kinetics of DNA desorption from MoS₂, WS₂ and GO after adding (A) 5 M urea, (B) 10 mM NaOH, (C) 3 M NaCl, (D) 50% DMSO, (E) 10 mM phosphate, and (F) 1 mM adenosine, The materials were added at 10 min indicated by the arrowhead.

Although electrostatic attraction is unlikely to take place between DNA and these materials, we still screened the charge interaction by adding 3 M NaCl. Indeed, we observed enhanced adsorption since the fluorescence slightly dropped for all the samples (Figure 4C). We next probed hydrophobic interactions by adding an organic solvent, DMSO, which can dissolve hydrophobic

molecules (Figure 4D). In this case, we also failed to see fluorescence enhancement for any material suggesting that hydrophobic interactions is insignificant for DNA adsorption.

DNA is made of nucleosides and a phosphate backbone, and DNA is known to use these chemical groups to interact with various materials. For example, DNA uses its phosphate to adsorb onto many metal oxides,⁴⁵ while uses its base coordination to bind to gold nanoparticles.⁴⁶ To probe possible chemical interactions, we next challenged the samples with 10 mM free inorganic phosphate or 1 mM adenosine. With phosphate, none of them showed much desorption, suggesting that the DNA does not use its phosphate backbone for adsorption. This is consistent with that the metal centers in the dichalcogenides are shielded. On the other hand, we observed a lot more desorption from GO upon adding adenosine. This is consistent with the fact that DNA is adsorbed on GO using its nucleobases (hydrogen bonding and pi-pi stacking).⁴⁷ The two dichalcogenides, however, failed to show much response to adenosine either, especially for WS₂.

Taken together, the above studies have ruled out hydrogen bonding, electrostatic attraction, hydrophobic interactions, and chemical interactions for MoS₂ and WS₂ to interact with DNA. As such, we reason that they adsorb DNA mainly via vdW force, which is a ubiquitous intermolecular/surface force. Using first principle density function theory (DFT), Vovusha and Sanyal indicated that all the four nucleobases interact with MoS₂ and WS₂ via vdW force, which is consistent with our conclusion.³⁵ They predicted that for individual nucleobases, the affinity on MoS₂ and WS₂ follows the order of G > A > T > C with atomic level details. For example, the H atom of the CH₃ group in adenine interacts with the S atom of the surface. For cytosine, the H of the CH₃ group and the O atom are relatively closer to the substrates. In another theoretical study, the vdW force was also deemed critical and order of interaction was determined to be G > A/C > T.³⁴ The fact that guanine adsorbs very tightly is also consistent with our observation in this study

(*vide infra*). MoS₂ and WS₂ sheets stack to form bulk materials via vdW force. The relatively large electronegativity between Mo/W and S can result in polarized electron distribution, which is favorable for vdW interactions (e.g. dipole and induced dipole interactions). Therefore, it is not surprising that these two materials mainly use vdW force for adsorbing DNA.

Our results above also suggest that the vdW force between DNA and GO is weaker than that between DNA and the dichalcogenides. For example, when urea was added to disrupt hydrogen bonding, much more DNA desorbed from GO. In the presence of urea, GO should still be able to interact with DNA via vdW force. As such, GO has much weaker vdW interactions with DNA.

DNA displacement by surfactants. After studying the force responsible for DNA adsorption by adding various denaturing agents, we next examined DNA displacement by other molecules. Such molecules do not denature DNA but they compete with DNA for the surface adsorption sites, which may further increase our fundamental understanding. First, we added various surfactants to displace adsorbed DNA. SDS is a small molecule anionic surfactant. While it had no effect on GO, ~10% DNA desorbed from the other two surfaces (Figure 5A). A slightly different trend was observed with CTAB, where desorption was observed only from MoS₂ (Figure 5B). With ten times higher CTAB (i.e. 0.1%), DNA also desorbed from WS₂, but still not from GO (Figure S1). Therefore, regardless of the charge of these small molecule surfactants, they both induced more desorption from the dichalcogenides.

We further tested two larger surfactant molecules: Tween 80 (Figure 5C) and Triton X-100 (Figure 5D). In both cases, the highest desorption occurred with MoS₂ and the least with GO, leaving WS₂ in between. This is consistent with that the surfactants interact with the dichalcogenides via their hydrophobic tails using vdW force to displace DNA. As such, the charge

on the surfactant headgroups is less important.⁴⁸ This is in direct competition with the adsorbed DNA since the same force was involved. On the other hand, GO adsorption is based on other forces and is thus less affected. It is also interesting to note that the higher molecular weight Tween 80 and Triton X-100 desorbed more DNA than the small molecule surfactants SDS and CTAB. This is likely due to the higher molecular weight surfactants (both are non-charged) having a stronger vdW force with the surfaces. The fact that DNA is adsorbed more tightly on GO when probed by surfactants, but less tightly on GO when probed by the denaturing agents also supports the importance of the vdW force on the dichalcogenides.

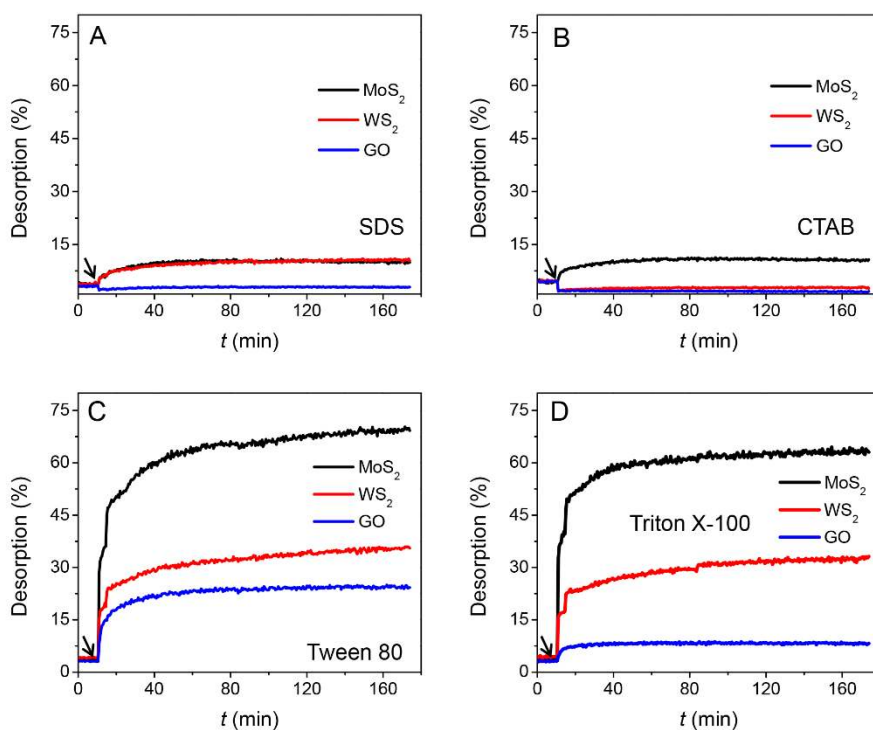


Figure 5. Kinetics of FAM-A₁₅ DNA desorption from MoS₂, WS₂ and GO after adding 0.01% (A) SDS, (B) CTAB, (C) Tween 80, and (D) Triton X-100. The reaction buffer contained 20 mM Tris, pH 7.0, 100 mM NaCl, and 2 mM MgCl₂. The surfactants were added at 10 min as indicated by the arrowheads.

Effect of DNA sequence and length. Since DNA adsorption by GO has been extensively studied,¹¹⁻¹⁵ this work is focused on MoS₂ and WS₂. Considering the similarity between MoS₂ and WS₂, we chose the latter to study the effect of DNA sequence and length. The four 15-mer FAM-labeled DNA homopolymers were respectively adsorbed on WS₂, and then Tween 80 was added to induce desorption. We observed the most desorption with C₁₅ followed by T₁₅, A₁₅ and G₁₅ (Figure 6A). Therefore, adsorption of the purines are stronger than the pyrimidines. This is consistent with the previous theoretical calculations of vdW force based DNA base adsorption.³⁴ Similarly, the effect of DNA length was studied using poly-A DNA. Interestingly, while longer DNA showed less desorption, the difference was quite small (Figure 6B). It might be that each DNA did not use all its bases to adsorb and the advantage of longer DNA is less obvious. For example, it has been simulated on graphene that ssDNA has two competing forces on the surface: inter-nucleobase stacking and nucleobase stacking with graphene.⁴⁹ The former force results in that only a fraction of the bases are adsorbed. A similar situation is likely to also occur on the dichalcogenide surfaces.

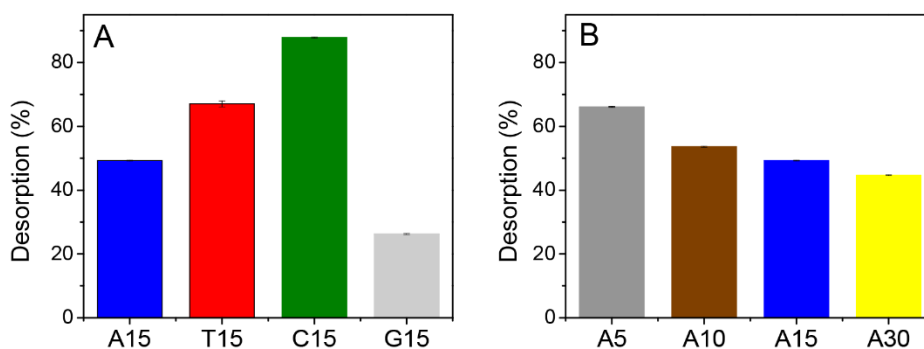


Figure 6. Effect of DNA sequence and length on DNA adsorption affinity on WS₂. Fluorescence measurement of (A) different sequences and (B) different lengths of FAM-labeled DNA desorption from WS₂ after 20 min incubation with 0.01% Tween 80. The reaction buffer contained 20 mM Tris, pH 7.0 with 100 mM NaCl and 2 mM MgCl₂.

DNA displacement by DNA. Since DNA is only physisorbed in this work, they can be displaced by other molecules, such as the surfactants demonstrated above. For DNA sensing applications, an interesting question is non-specific DNA displacement by DNA. To study this, we adsorbed FAM-A₁₅ and then added its cDNA, T₁₅ or the same A₁₅ DNA but without the fluorophore label. For MoS₂ and WS₂, we observed more fluorescence signal when T₁₅ was added, suggesting that DNA hybridization plays a key role here. Non-specific displacement by A₁₅ also occurred, but to a smaller extent. However, more displacement by A₁₅ occurred on GO than hybridization by T₁₅, which is consistent with our previous observation.⁵⁰ This is an important difference, and suggests that A₁₅ adsorption by GO might be more favorable than its hybridization with T₁₅. On the other hand, DNA adsorption by the dichalcogenide surfaces is weaker to allow DNA specific hybridization to be the dominating interaction.

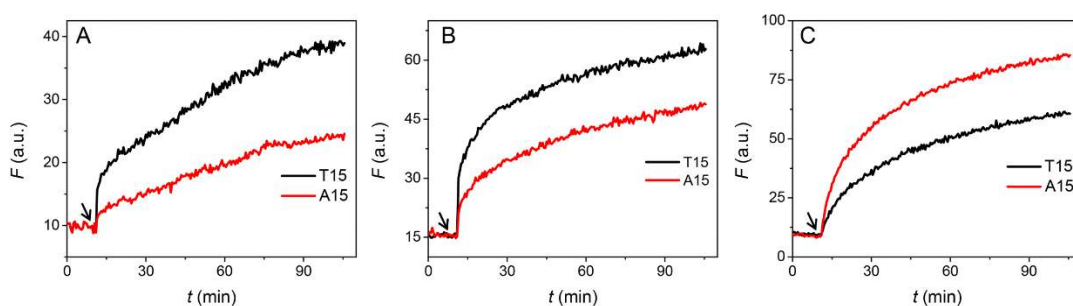


Figure 7. DNA hybridization and displacement. The FAM-A₁₅ DNA probe was first adsorbed by each surface and then a non-labeled T₁₅ or A₁₅ DNA was added to induce probe desorption from (A) MoS₂, (B) WS₂, and (C) GO. The DNA was added at 10 min indicated by the arrowheads.

DNA sensing with a random sequence. After these fundamental surface science studies, we next compared the analytical performance of these materials for DNA detection. Our sensing scheme is shown in Figure 8A. A fluorescent probe DNA was first adsorbed and its cDNA was added to

induced signaling.²⁷ The above studies in Figure 7 used two model DNA homopolymer sequences for mechanistic studies. Here we employed a random sequence for testing analytical performance. The kinetics of signaling on each surface are shown in Figure 8B-D, respectively. They all showed cDNA concentration dependent fluorescence enhancement, thus supporting potential sensing applications. We quantified the relative fluorescence enhancement at 10 min after adding the cDNA (Figure 8E). The GO sample showed the strongest signal enhancement reaching ~18-fold, while the other two had a similar performance of ~4-fold. A similar trend was observed when a different probe DNA sequence was used (Figure S2). The slope of the initial linear increase was compared (Figure 8F), and the GO sample is 4.3-fold more sensitivity (note this slope is the sensitivity of the sensors). We also calculated the detection limits of these sensors based on the signal greater than 3 times of background variation, and they turned out to have a similar detection limit (Figure 8G). This is likely due to a less fluctuated background to compensate for the lower sensitivity of the dichalcogenates. While cDNA-concentration-dependent response has been demonstrated, such sensors may suffer from non-specific displacement by other molecules and thus produce false positive signals. Therefore, careful controls and internal references are needed to ensure correct analytical interpretations. For example, by co-adsorbing a random DNA labeled with a different fluorophore as an internal standard, it is possible to identify false positive signals due to non-specific probe displacement.⁵¹ Covalent linking is another strategy,⁵² which however has yet to be developed for the dichalcogenates.

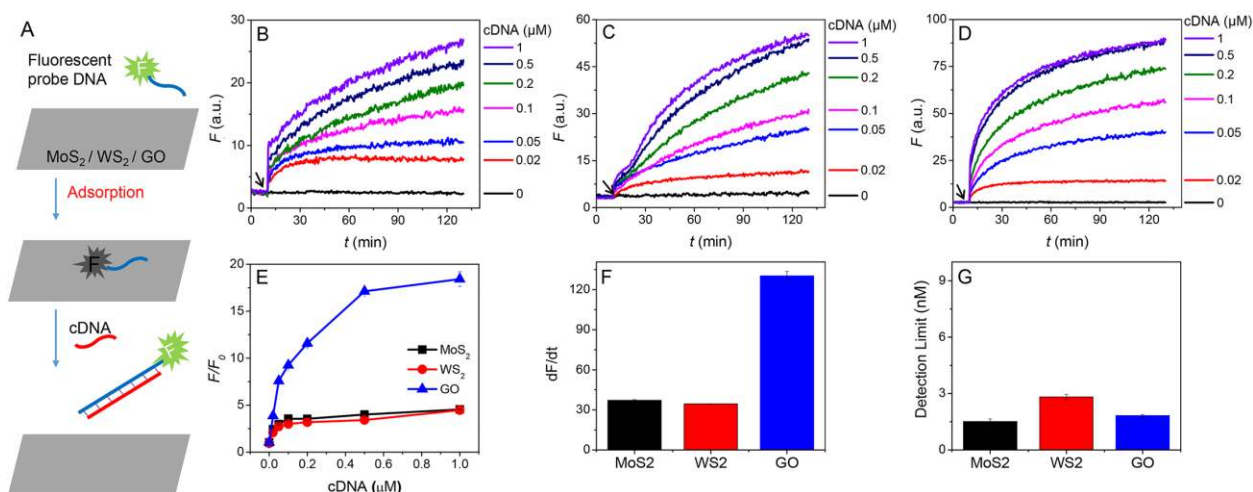


Figure 8. Schematics of DNA sensing using a fluorophore-labeled DNA probe. The probe is adsorbed by MoS₂, WS₂ or GO, resulting in fluorescence quenching. After adding the target cDNA, fluorescence is recovered due to DNA hybridization. Kinetics of probe desorption from (B) MoS₂, (C) WS₂ and (D) GO in the presence of various concentrations of cDNA. The arrowheads indicate the time point when cDNA was added (10 min). (E) The relative fluorescence enhancements of MoS₂, WS₂ and GO after 10 min reaction. (F) The slope of the initial linear signal increase in (B-D) indicative of sensor sensitivity. (G) The detection limits of the three sensors from (B-D).

Conclusions

In summary, we compared DNA adsorption and desorption from three representative 2D materials: GO, MoS₂ and WS₂. In particular, fundamental surface forces were probed by various chemicals, and the implication for DNA sensing was emphasized. We measured the zeta-potential of each material and they were all negatively charged. As a result, DNA adsorption requires a high ionic strength to screen charge repulsion. While GO, MoS₂ and WS₂ can all adsorb DNA and quench the fluorescence of the adsorbed fluorophore, the mechanism of DNA adsorption on each material

is quite different. DNA is adsorbed on GO mainly via pi-pi stacking and hydrogen bonding, while MoS₂ and WS₂ rely on vdW force as probed by various denaturing conditions. Denaturing agents such as urea and strong base induced more DNA desorption from GO, while all the tested surfactants are more effective to displace DNA from the two dichalcogenides. Using FAM-A₁₅ as a probe, T₁₅ induced more probe desorption than A₁₅ on MoS₂ and WS₂, suggesting specific DNA hybridization. The opposite however was observed on GO, suggesting non-specific displacement. When their performance for DNA detection is compared, the GO surface had the highest sensitivity, while the detection limit of the three sensors turned out to be similar. These fundamental understandings are valuable for designing and optimization of sensors and devices based on DNA and 2D materials.

Supporting Information Available

This information is available free of charge via the Internet at <http://pubs.acs.org/>.

DNA desorption by high concentration of surfactants and additional DNA sensing data (PDF).

Acknowledgement

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